Sunday Afternoon, October 28, 2001

Biomaterials Plenary Session
Room 102 - Session BI-SuA

Biomaterials Plenary Session

Moderator: M. Grunze, University of Heidelberg, Germany

3:00pm **BI-SuA1 Living Nightmares: Facing the Growing Threat of Biological Weapons***, S. Block,* Stanford University **INVITED**

Please submit an abstract.

3:40pm **BI-SuA3 Protein Biochips: Powerful New Tools to Unravel the Complexity of Proteomics***, P. Wagner,* Zyomyx Inc. **INVITED**

Novel high-throughput biological applications in the drug discovery process, disease diagnosis, and the development and application of patient-specific medicines require highly parallel, miniaturized device technology applied to proteins and their biochemical pathways. While technological innovation has adapted the analysis of genetic material to a miniaturized format, the more delicate nature of protein structures has precluded the development of analogous devices for proteins. Protein biochips have started to emerge recently based on new developments and integration efforts in advanced materials, protein engineering, and detection physics. Recent developments and selected examples will be presented with an emphasis on the technical challenges in surface and assay methodologies.

4:20pm **BI-SuA5 The Biocompatibility Challenge: Arterial Interfaces in 2001***, R.S. Schwartz,* Mayo Foundation **INVITED**

The lack of a suitable prosthetic arterial conduit remains a major problem in clinical medicine today. The breadth of such a need is immense in scope, encompassing peripheral vessels, cerebral arteries, and coronary arteries and grafts. Problems such as restenosis of both coronary stents and following stenting will be shortly solved. The principal mechanism of instent restenosis is by neointimal hyperplasia forming in injured arteries after oversized coronary stents. The cellular events of neointima occur in 3 stages: Thrombus formation occurs after injury (generally less than 24 hours), with fibrin-rich thrombus accumulates around the platelet site. The second stage is cellular recruitment, where the thrombus develops cells having the appearance of endothelial cells. Cell infiltration consists of monocytes and lymphocytes. The third stage is proliferative, occurring late with actin-positive cells colonizing the thrombus from the lumen, forming a "cap" across the top. The cells progressively proliferate toward the injured media, resorbing thrombus until it is gone and replaced by neointimal cells. In coronary models, denudation of endothelium alone does not cause neointimal formation. It is only when the internal elastic lamina is disrupted and media injured that neointima occurs. We hypothesize that the media plays an important role in limiting neointimal hyperplasia and believe in the importance of normal medial cells to limit neointimal hyperplasia. If a "living stent" could be made with medial cells present, neointimal limitation might be possible. Such as stent would represent a short segment of "total artificial artery", placed over artery injury sites to function immediately as a new vessel. We are developing such a stent with porcine carotid smooth muscle cells. The cells are grown in culture into a stent with a three-dimensional matrix. The cells may be transfected with a marker gene (GFP) and re-implanted into the coronary arteries 3 weeks later. Early studies show cell survival within the stent, with strong GFP expression. Such a "living stent" may have application for limiting neointima. Moreover, if the techniques are successful, this would represent a step toward the artificial artery.

NBS-NIST Centennial
Room 120 - Session NB-SuA

NBS/NIST Centennial

Moderator: C.J. Powell, National Institute of Standards and Technology

5:00pm **NB-SuA7 Vacuum Measurements at NBS/NIST***, B.R.F. Kendall,* Elvac Laboratories **INVITED**

Almost from its inception, NBS (National Bureau of Standards) began improving the existing techniques for producing and measuring high vacuum. By the 1920s and 1930s this expertise was being put to use in several state-of-the-art electron and ion beam devices, especially in early mass spectrometers where minimum beam scattering was essential. This began the long series of refinements of vacuum gauges and their associated operating procedures, ranging from the relatively mundane McLeod gauges of the early era to the spinning rotor gauges, residual gas analyzers and advanced laser photoionization detectors of today. Important advances were also made in the design and calibration of standard leaks, flowmeters and related equipment. A number of valuable workshops were organized to bring together researchers in many of these areas, and also to introduce users to advanced devices such as the spinning rotor gauge. As the organization evolved into the present-day NIST (National Institute of Standards and Technology), support was also given to outside researchers working on fundamental pressure-dependent phenomena such as molecular collisions and electron lifetimes. At the same time, NBS/NIST has also become involved in areas of vacuum technology far removed from those conventionally covered by the AVS, such as precision altimetry and the problems of introducing vacuum at the milliTorr level to the refrigeration industry. Valuable contributions continue to be made in the areas of calibration, elimination of sources of error in vacuum measurements, and the development of new vacuum standards.

5:40pm **NB-SuA9 Highlights of Surface Science at NBS/NIST: Accomplishments and Impacts***, T.E. Madey,* Rutgers, The State University of New Jersey **INVITED**

This will be a selected summary of important accomplishments and "firsts" at NBS/NIST through the years in many areas of surface science: instrument development, original experiments, standards development, and theory. Seminal developments and achievements with lasting impacts will be emphasized (including, but not limited to, experiment and theory of field emission tunnel resonances, the topografiner as a predecessor of STM, high-performance electron-energy analyzers, spin-polarized electron detection and SEMPA, novel miniature gas sensors, improved devices based on the giant magnetoresistance effect, ESDIAD, catalysis over single crystals, laser-induced desorption, surface vibrational lifetimes, molecular modeling of time-dependent phenomena at surfaces, inelastic neutron scattering from adsorbates, calculation of electron inelastic mean free paths, development of databases and reference materials).

NBS-NIST Centennial
Room 121 - Session NB-SuP

NBS/NIST Centennial

Moderator: C.J. Powell, National Institute of Standards and Technology

NB-SuP1 Resonance Tunneling: from Field Emission to Molecular Electronics with Intermediate Stops; a Thirty Five Year NBS/NIST Saga*, J.W. Gadzuk,* National Institute of Standards and Technology

Initiation of the modern era of surface science is generally acknowledged to have occurred in the 1960's, a period marked by the recognition and development of measurement and theoretical techniques for studying surface properties and processes on the (single!) atomic level. Resonance tunneling of field emitted electrons through adsorbates on metal surfaces reported in a 1969 NBS paper was the first-ever work in which the electronic energy level spectra of adsorbed atoms was observed and theoretically interpreted (as "skewed" Fano profiles).@footnote 1,2@ Variants and extensions of the theory have formed the basis for subsequent NBS/NIST studies of resonant tunneling/scattering phenomena involved in desorption,@footnote 3@ basic STM operation,@footnote 4@ quantum wells,@footnote 5@ scanning tunneling spectroscopy of Kondo systems,@footnote 6@ and molecular electronics.@footnote 7@ A useful synergism amongst these studies illustrates the positive consequences of a long-term commitment to the search for varied realizations of a common fundamental process (here resonance tunneling). Fortunately this research strategy has been possible at NBS/NIST throughout much of its first 100 years.@footnote 8@ @FootnoteText@ @footnote 1@ E.W.Plummer, J.W.Gadzuk, and R.D.Young, Solid State Comm.7(1969)487. @footnote 2@ J.W.Gadzuk and E.W.Plummer, Rev.Mod.Phys. 45(1973)487. @footnote 3@ J.W.Gadzuk, Phys.Rev.B44(1991)13466. @footnote 4@ J.W.Gadzuk, Phys.Rev.B47(1993)12832. @footnote 5@ A.Bringer, J.Harris, and J.W.Gadzuk, J.Phys.:Condens.Mat.5(1993)5141. @footnote 6@ M.Plihal and J.W.Gadzuk, Phys.Rev.B63(2001)085404. @footnote 7@ A.Aviram and M.Ratner, Chem.Phys.Letters 29(1974)277. @footnote 8@ A Century of Excellence in Measurements, Standards, and Technology, NIST Special Publication 958, ed. by D.R.Lide(2001).

NB-SuP2 Scanning Tunneling Microscopy in the Electron Physics Group at NIST@footnote 1@*, J.A. Stroscio,* *E.W. Hudson, R.J. Celotta, D.T. Pierce,* National Institute of Standards and Technology

The history of scanning tunneling microscopy in the NIST Electron Physics Group (EPG) spans more than 3 decades. In this poster presentation we will document the development of scanning tunneling microscopy in the EPG group, starting back in the 1960's when Russell Young developed the "Topografiner", and continuing to the present where state-of-the-art measurements are made with a scanning tunneling microscope operating at 2 K and in magnetic fields at 10 T. @FootnoteText@ @footnote 1@This work is supported in part by the Office of Naval Research.

NB-SuP3 Spin-Polarized Electrons at NBS/NIST@footnote *@*, D.T. Pierce,* *R.J. Celotta, J. Unguris,* National Institute of Standards and Technology

Over the past 25 years, the NIST Electron Physics Group has pioneered the use of spin-polarized electron measurement techniques in condensed matter and atomic physics. The work began with the development of an electron gun, based on photoemission from negative electron affinity GaAs, which produced an intense beam of electrons with easily reversible spin polarization. This allowed us to make sensitive surface magnetometry measurements such as polarized electron scattering and spin-polarized low-energy electron diffraction (SPLEED) measurements of magnetic surfaces. The spin-polarized electron gun enabled us to demonstrate the first spin-polarized version of inverse photoemission spectroscopy (SPIPES) and allowed others to add spin polarization to several surface measurement techniques including electron energy loss spectroscopy (SPEELS) and low energy electron microscopy (SPLEEM). We also developed a compact, efficient spin analyzer that is particularly well suited to measure the spin polarization of secondary electrons emitted from magnetic samples in a scanning electron microscope. This measurement technique, known as scanning electron microscopy with polarization analysis (SEMPA), provides high-resolution images of surface magnetization. SEMPA measurements have proven powerful for investigating both fundamental problems, such as interlayer exchange coupling of magnetic multilayers, and technological questions, such as the magnetic microstructure of small magnetic device elements. We describe a new SEMPA instrument designed to meet the magnetic imaging challenges of the near future. @FootnoteText@ @footnote *@Supported in part by the Office of Naval Research.

NB-SuP4 Investigations of Electron Emission and Scattering Phenomena at Surfaces*, C.J. Powell,* National Institute of Standards and Technology

An overview will be given of almost four decades of work at NBS/NIST in which different phenomena associated with electron emission from surfaces and electron scattering by surfaces were investigated. These investigations, made with many coworkers, range from analyses of energy-loss spectra from liquid metals to studies of different Auger-electron lineshapes, reviews of electron attenuation lengths and inner-shell ionization cross sections, interlaboratory comparisons of AES and XPS peak energies and intensities, investigations of correlation effects in inner-shell excitations, calculations of electron inelastic mean free paths, investigations of elastic-electron scattering effects in AES and XPS, measurements of electron attenuation lengths, development of improved procedures for the calibration of binding-energy scales of XPS instruments, development of standard test data for XPS, and development of NIST databases for applications in XPS and AES.

NB-SuP5 Application-Tunable Chemical Microsensors: Multicomponent Research for New Measurement Technology*, S. Semancik,* *R.E. Cavicchi, M.C. Wheeler, N.O. Savage, C.J. Taylor,* National Institute of Standards and Technology

For more than 15 years, NIST has been involved in fundamental surface science, thin film science, and sensor science studies directed at advancing solid state chemical sensing technology toward new levels of performance and reliability. Adsorption-induced property changes occurring at the surfaces of thin films have been investigated and employed for detecting and quantifying a wide range of gases and vapors with microscale devices. Tunability for varied applications has been realized through the use of multielement arrays with sensing films of differing composition, and individually adjustable operating temperatures. In this presentation we review efforts in our program, with an emphasis on key interfacial phenomena, as well as on vacuum-based materials processing and characterization. Research to be described includes examination of: vacancy defects in oxide semiconductors (which set base conductance levels for conductometric gas sensing films), micromachining of Si (to produce low power device platforms - "microhotplates"), thermally-activated CVD (to incorporate sensing materials into microscale structures), correlations between adsorbed species and interfacial electronic transport, temperature-driven adsorbate transient phenomena, and microscale chemical cross-talk. In addition, we illustrate the utility of the microhotplate array platforms as research tools for combinatorial optimization of the compositions and microstructures of sensing film materials, and investigation of gas-surface interactions.

NB-SuP6 The NIST Synchrotron Ultraviolet Radiation Facility*, U. Arp,* *M.L. Furst, E.W. Hagley, T.B. Lucatorto, C.S. Tarrio, C.W. Clark,* National Institute of Standards and Technology

In 1961 NBS established the first dedicated synchrotron radiation source, the Synchrotron Ultraviolet Radiation Facility (SURF). The first experiment performed at SURF, two-electron photoexcitation of He, created significant excitement in the world of atomic physics, and demonstrated the utility of synchrotron radiation for performing experiments in the vacuum ultraviolet and beyond. The SURF synchrotron, designed for nuclear physics experiments, was converted to the SURF II electron storage ring, which is more suitable as a radiation source. A SURF II - SURF III upgrade, accomplished in 1998, involved replacement of the original synchrotron magnet with a new magnet for improved field uniformity and higher energies, and an enhanced radio-frequency system for more stable operation. SURF III plays a key role in synchrotron-based radiometric metrology at NIST, especially in the DUV and EUV regions of the spectrum, for three reasons. First, SURF’s optical output is easily calculable from first principles. This characteristic is related to the fact that it has a perfectly circular orbit. Second, SURF can operate stably over a wide range of electron energies, from below 100 MeV to 380 MeV, which allows one to tune the wavelength of peak output over different regions of the DUV and EUV and thus minimize effect of out-of-bandwidth radiation. The third relates to the stability of the continuous output. Since 1967 SURF has been used to provide calibration services, starting with the calibration of standard detectors in the UV spectral region. Since then several other metrological activities have been implemented at SURF III beamlines. Beamline 2 is home to a spectrometer calibration facility, which allows users to calibrate space-borne photodetector packages in the wavelength region from 1 nm to 400 nm with an accuracy of less than 1 %. Beamline 3 is currently being developed as the U.S. National Standard for the calibration of standard light sources in the air UV from 200 nm to 400 nm.

Beamline 4 provides us with the ability to calibrate standard detectors in the region from 120 nm to 320 nm in support of the U.S. National UV scale. Beamline 7 provides characterization of thin-film multilayer EUV mirrors, having the unique capability of handling mirrors as large as 450 mm, which is especially relevant to the developers of EUV lithography. Beamline 9 provides the Nation's standard for detectors in the region from 5 nm to 50 nm, in continuation of the program started in 1967.

NB-SuP7 Surface and Microanalysis Science Division: From XPS Standards to Near-field Optical Microscopy.*, **R.R. Cavanagh**, S.J. Stranick, C.A. Michaels,* National Institute of Standards and Technology

The Surface and Microanalysis Science Division at NIST has worked with the AVS community over the years to develop the measurement science that underlies a range of surface measurements. Key activities have included theoretical and experimental efforts ranging from the modeling of inelastic electron scattering events at surfaces, studies of ion, electron, and photon induced surface reactions, and optical probes of buried interfaces, to energy and state and time-resolved studies of the dynamics of surface processes. Recent efforts have investigated the use of near-field optical methods to combine spectroscopic contrast with the spatial resolution of scanned probe methods. We have developed an infrared near-field scanning optical microscope that incorporates a tabletop femtosecond laser-based infrared source with an illumination mode apertured probe. The application of the near field infrared instrument to thin homopolymer films, to blends of polyethylacrylate and polystyrene, and to titanium dioxide particles with acrylic melamine will serve to illustrate the utility of this method for characterizing chemical nanostructures.

NB-SuP8 Surface Science at the NBS / NIST SURF-II Synchrotron Light Source*, **R.L. Kurtz**,* Louisiana State University*; T.E. Madey,* Rutgers, The State University of New Jersey*; R.L. Stockbauer,* Louisiana State University

A retrospective of surface science experiments performed at the NIST SURF-II synchrotron for the time period of 1980 to the early 1990's will be presented. The measurements that were performed during that time period included a range of photoemission and stimulated desorption studies of surfaces. Among the standards measurements, a technique was developed to measure quantitative electron mean-free paths in condensed molecular solids. Other studies that were conducted applied photoemission to evaluate the oxidation of metals and the adsorption of simple molecules on metals and oxides. Stimulated desorption was the focus of a number of other experiments from both metals and oxides and a collection of data from a range of these measurements will be presented.

NB-SuP9 Cluster SIMS Research at NIST*, **J.G. Gillen**,* National Institute of Standards and Technology

Secondary ion mass spectrometry (SIMS) is a widely used technique for the determination of both the surface and in-depth elemental and molecular composition of a wide variety of solid materials. The National Institute of Standards and Technology has been at the forefront of SIMS research for nearly 30 years. A major recent activity at NIST has been the development and application of Cluster SIMS. In SIMS, the surface to be analyzed is bombarded in ultrahigh vacuum with an energetic ion beam (typically Ar@super +@, O@sub 2@@super +@, Cs@super +@ or Ga@super +@) with subsequent detection of characteristic sputtered secondary ions by mass spectrometry. In the Cluster SIMS approach, the standard ion beams are replaced with small polyatomic or cluster primary ions such as SF@sub 5@@super +@ or C@sub 10@@super -@. When a cluster ion strikes a surface with several keV of energy, it dissociates into its constituent atoms with each constituent retaining a fraction of the initial energy. The reduction in impact energy results in a reduced penetration depth below the surface and the possibility for improved SIMS depth resolution. The dissociation of the cluster ion also leads to a localized deposition of energy in the near-surface region of the sample that may enhance the yield of characteristic molecular ions by several orders of magnitude providing greater sensitivity for organic surface characterization. Research at NIST in Cluster SIMS covers the range from ion source development to demonstration of Cluster SIMS advantages in applications to semiconductors, polymers, and biomolecules.

NB-SuP10 Triply Differential Photoelectron Spectroscopy at SURF-II*, **R.L. Stockbauer**,* Louisiana State University*; D.L. Ederer,* Tulane University*; J.B. West,* Daresbury Laboratories*; K. Codling,* Reading University*; A.C. Parr,* NIST*; J. Dehmer,* NSF

Starting in 1979, we developed a sophisticated spectrometer that was used to make angularly and vibrationally resolved photoelectron measurements. The studies concentrated on resonance phenomena in gas phase atomic and molecular systems. The initial instrument utilizing a single spectrometer was replaced with a dual spectrometer system in the early 1980s. These instruments were used to obtain detailed vibrationally resolved information on the effects of shape resonances and autoionization on the distribution of the final states of the molecular ion. We were the first to report striking non-Franck-Condon intensity distributions associated with a shape resonance in N@sub 2@. Subsequent studies uncovered unusual intensity distributions in the vibrationally resolved spectra that could not be directly explained by predictions of traditional calculations of molecular photoionization. The high resolution and sensitivity of the NIST spectrometer enabled the identification of a new Rydberg series in O@sub 2@. The most comprehensive data set was taken on the CO@sub 2@ molecule, discovering forbidden interactions between vibrational bending and stretching modes. We will review the highlights of over a decade of work.

NB-SuP11 Future Directions of Vacuum and Low Gas-Flow Metrology at NIST*, **A. Lee**, J.P. Looney, A.P. Miiller, P.J. Abbott,* National Institute of Standards and Technology

The vacuum and low-flow metrology project areas at NIST develop and maintain standards to disseminate the highest measurement capability to US industry, advance measurement science, and establish international measurement comparability. In the years to come, we plan to: Introduce New Measurement Standards: - Investigate intrinsic pressure standards based on material fixed points and atomic calculations - Extend spinning rotor gauges ~10@super -7@ Pa, potentially replacing ion gauges entirely as secondary standards - Develop in-situ, non-intrusive flow calibration techniques for reactive gases and vapors in semiconductor fabrication - Offer a leak-into-atmosphere calibration service and extend the range of the leak-into-vacuum service (applications OLED-substrate permeation, refrigeration, nuclear containment, pressure vessels, etc.) - Develop primary oil manometers utilizing a 4-color column-height determination scheme - Create an on-demand SRG calibration service via provision/exchange of calibrated rotors Improve Current Standards and Measurement Capabilities: - Reduce uncertainties in our orifice flow standard by nearly an order of magnitude - Work with industry to make RGAs more reliable and quantitative instruments - Offer on-site proficiency testing of mass flow controllers, and thermophysical data on new electronic gases Ensure Measurement Comparability: - Continued leadership in international, regional and domestic comparisons of measurement standards - Improve the vacuum metrology capability of the SIM region - Develop a real-time capability to remotely operate and observe instruments under calibration or testing

Applied Surface Analysis
Room 134 - Session AS-MoM

Quantitative Analysis and Data Interpretation I: SIMS

Moderators: D.W. Moon, Korea Research Institute of Standards and Science, M.P. Seah, National Physical Laboratory

9:40am **AS-MoM1 TOF-SIMS Characterization of Additives in Polymer Materials: Influence of Primary Ion Bombardment Conditions***, **R. Kersting**, B. Hagenhoff,* TASCON GmbH, Germany

Additives are an essential part of polymer formulations because they decisively influence the chemical behavior of daily polymer products. Whereas many analytical techniques exist to analyze additives in the polymer bulk, only a few techniques are able to obtain chemical information on the polymer surface, among these Time-of-Flight Secondary Ion Mass Spectrometry. Many studies have proven the general usefulness of TOF-SIMS analysis for the characterization of polymer materials and polymer additives. However, systematic investigations on the optimum analytical conditions for a sensitive detection of additives from polymer surfaces are still sparse. We therefore investigated the influence of the primary ion bombardment parameters on the emission behavior of model samples. The samples were prepared by spin coating the antioxidant Irganox 1010 in different concentrations onto additive free LDPE substrates. The secondary ion parameters yield, disappearance cross-section and secondary ion emission efficiency (yield per damaged area) were determined for primary ion bombardment with Ga@super +@, Cs@super +@, and SF@sub 5@@super +@. The primary ion energies were varied between 4 and 10 keV for SF@sub 5@@super +@ and Cs@super +@ and between 5 and 25 keV for Ga@super +@ bombardment. From these experiments optimum analytical conditions for the analysis of thin additive coatings on polymer materials were deduced. The results will be applied to real world polymer surfaces with respect to additive quantification and additive degradation processes.

10:00am **AS-MoM2 ToF-SIMS Surface Chemical State Imaging of Biomaterials***, B.T. Wickes, **D.G. Castner**,* University of Washington

New developments in molecular biology and materials science are now being applied to designing molecular specificity and recognition into the surface of biomaterials. These novel surfaces are envisioned to have a well-defined array of recognition sites designed to interact specifically with proteins and cells. The development of surface analysis techniques that will provide detailed chemical state information at high spatial resolution is required to investigate the presentation of these recognition sites on a biomaterial surface. Static ToF-SIMS has the potential to provide detailed information about the chemical surface structure of biomaterials with a spatial resolution of 1 micron. However, static ToF-SIMS images containing a full mass spectrum at each pixel can be complex to analyze. The challenge is to develop a method for determining all chemical species present in the surface region along with their location and concentration without a priori knowledge about the sample. Image analysis can be considered to be a 3 step process of denoising, component identification, and image reconstruction. A gold surface patterned with 2 micron lines of ethylene glycol thiol molecules separated by 2 micron lines of fluorinated thiol molecules was used as a model system to evaluate different imaging processing strategies. Effectiveness of various denoising methods (wavelet, boxcar, median, etc.) was evaluated in terms of removing speckle noise, preserving image features, and the time required for denoising. Principal component analysis was used to identify the combination of mass fragments that provided the best image contrast.

10:20am **AS-MoM3 Application of Spectrum Imaging and Multivariate Statistical Analysis to Time-of-Flight Secondary Ion Mass Spectrometry@footnote 1@***, **J.A. Ohlhausen**, M.R. Keenan, D.E. Peebles, P.G. Kotula,* Sandia National Laboratories

The combination of spectrum imaging and multivariate spectral image analysis for information extraction have recently been applied as powerful new phase mapping tools in a variety of materials characterization techniques. In this process, an image is collected by acquiring an entire spectrum for each pixel of the image. Subsequently, multivariate spectral image analysis is applied to the image data to obtain the primary component spectra from each significant phase present in the image. Finally, the distribution of each phase may be obtained from the initial image and primary component spectra to provide a detailed phase mapping of the surface composition. No subjective guesses as to the identity of phases believed to be present are required to complete the phase identification and mapping process, and much of the spectral noise is removed from the image. Instead, the robust statistical process is able to unambiguously identify all of the spectral features uniquely associated with each distinct phase throughout the image, providing information well beyond that contained in a series of traditional image maps. In this work, this new approach is applied to Time-of-Flight Secondary Ion Mass Spectrometry (TOF SIMS) images, illustrating the power and advantages of precise phase identification and imaging for a number of representative sample materials.

10:40am **AS-MoM4 Multivariate Statistical Approaches for Distinguishing Between Chemical and Topographical Features in TOF-SIMS Images***, **B.J. Tyler**,* University of Utah

Despite its many strengths, TOF-SIMS imaging presents the analyst with several formidable challenges. One of the most notable of these challenges is differentiating between chemical and topographical effects. The intensity of ion signals depends not only on the surface composition but also upon the surface height and inclination (topography) and the material beneath the surface (matrix). These effects can be particularly dramatic on insulating samples where topography may result in a distortion of the electric field. In many cases, the intensity variations due to the structure of the sample can obscure features associated with surface chemistry. We have been involved in quantifying the effects of topography on TOF-SIMS images and exploring multivariate statistical methods that can be used to deconvolve chemical and topographic effects. Images of surfaces with strong topographic features, including fibers, spherical particles, and trenches will be presented. The influence of these topographic features on the absolute and relative peak intensities has been explored on conducting and insulating surfaces. We have found that when images are generated by rastering the ion beam, topography can cause severe distortions in the image. For example, spikes on the surface can appear as thin stripes in the image. Particles can create field lines that result in repressed ion emission causing a halo surrounding the particles. Multivariate statistics can help reduce some but not all of these effects on the images. Results will be presented using principle components analysis and mixture models to process images with confounding chemical and topographical features.

11:00am **AS-MoM5 Data Interpretation and Quantitative Analysis - A Global Approach in Static SIMS***, **I.S. Gilmore**, M.P. Seah,* National Physical Laboratory, UK **INVITED**

Static SIMS spectra are rich in information but their complexity is an acknowledged barrier to the wider take up of the technique in industry. To identify an unknown material using static SIMS, an analyst needs to compare the measured spectrum with those available in spectral libraries. However, existing spectrometers use a wide variety of instrumental geometries, primary ion species and operating energies. Consequently, data from different laboratories differ significantly and data in handbooks and libraries are only broadly comparable. Additionally, existing libraries (1250 spectra) are small compared to those used in organic mass spectrometry (356000 spectra) and are tiny in comparison to the industrial need. A strategy of methods is required to interpret and quantify spectra of unknown materials. For those instances when reliable spectra are contained in libraries, multivariate and artificial neural network approaches can give accurate identification and quantitative information. These methods will be discussed and compared. However, if the material is not in the library as is generally the case, an entirely new method, known as G-SIMS or gentle-SIMS@footnote 1@ is fruitful. This method gives relatively simple spectra whose peaks are directly related to the molecules present and their main constituents. These spectra may be interpreted without a library. These approaches may be combined to form a global strategy for the analysis of a wide range of surfaces. @FootnoteText@ @footnote 1@I S Gilmore and M P Seah, Appl. Surf. Sci. 161 (2000) 465.

11:40am **AS-MoM7 Secondary Ion Mass Spectrometry Analysis of Wafer Contamination Resulting from Gloved Hands***, W.R. Morinville, **C. Blackmer**,* Micron Technology, Inc.

It is well known that wafer-handling protocols to avoid contamination are a mandatory part of semiconductor fabrication. One of the most significant pieces of the standard "cleanroom" suit is the glove worn to eliminate contamination from human skin, of which mobile ions from fingerprint oils are a major contributor. Once the glove is in place, it is often considered unnecessary to use appropriate tools when the wafers are to be submitted for testing or analysis. This paper will show that wafer handling, even with fabrication recommended gloves in place, still significantly contaminates the wafer. The study began with a prime Si wafer that was divided into sections for experimentation. One piece of the wafer was not touched and would become the control sample. The remaining pieces were touched with bare hands along with various gloves that were all approved for use in a fabrication environment. An intriguing observation was that fingerprint-like marks were visible in all cases where the wafer had been touched. Secondary Ion Mass Spectrometry was then utilized to analyze the fingerprinted areas. Mobile ion contamination was found to be associated with many of the gloves in the study. It was also verified that the contamination was coming from the glove itself and not diffusing through the glove from the hands.

Biomaterials
Room 102 - Session BI-MoM
Molecular Recognition

Moderator: K.E. Healy, University of California, Berkeley

9:40am **BI-MoM1 Chemical Recognition on Lipid Membrane Surfaces***, **D.Y. Sasaki**,* Sandia National Laboratories **INVITED**

Cell communication and sensing are processes mediated by chemical recognition events that occur on the lipid membrane surface. Chemical signals in bulk solution are recognized by membrane receptors, which subsequently organize into specific structures that activate signal cascades. Through a biomimetic approach, we have examined chemically induced molecular reorganization events in lipid membranes in an effort to learn how to control this process for sensor applications and nanoscale architecture. By using a synthetic approach we have simplified interactions between molecular species to evaluate their effects on molecular reorganization. Simple two-component lipid bilayer assemblies were prepared with receptors for heavy metal ions, proteins, and polypeptides. The aggregational state of these fluorophore-labeled receptor molecules, as they responded to chemical recognition events, were monitored globally by spectroscopic means (e.g., excimer formation of pyrene labels) and locally via in situ atomic force microscopy (AFM). We found that the dispersion and aggregation of receptors in a bilayer can be directed through multiple levels of interactions, such as electrostatic charge from metal ion chelation, multiple-point binding interaction with polyfunctional guests, and phase separation. In situ AFM studies observed that nanoscale structures composed of aggregated receptors but could be made to disappear or reappear upon the addition or removal of specific chemical ligands. At a slightly larger scale, the functionalized bilayers displayed a unique ability to self-assemble into hierarchical structures of stacked bilayers through a process mediated by chemical recognition. These lipid bilayers with their unique optical response, biocompatibility, and self-organizational properties demonstrate a versatile array of possibilities for sensing and nanoarchitecture.

10:20am **BI-MoM3 Surface Docking Sites for Macromolecules: Interface Architecture based on PLL-g-PEG/PEGbiotin-(Strept)avidin**, ***N.-P. Huang**, J. Vörös, S.M. De Paul, M. Textor, N.D. Spencer,* ETH Zürich, Switzerland

Surface docking sites (nanoscale islands) are desirable for the specific adhesion of macromolecules, such as proteins and oligonucleotides, onto surfaces. The surrounding areas of such docking sites should be non-adhesive so that the adsorbed macromolecules are prevented from denaturing after adsorption. We have mixed poly(L-lysine)-g-poly(ethylene glycol) (PLL-g-PEG) and a variant of PLL-g-PEG in which some of the PEG chains are biotinylated (PLL-g-PEG/PEGbiotin) to form a novel polymeric interface, in order to tailor chip surfaces in terms of non-specific and specific analyte-surface interactions. By means of optical waveguide lightmode spectroscopy (OWLS), streptavidin and avidin are shown to bind specifically to the biotin-functionalized PEG, while the resistance of the remaining PEG chains to protein adsorption yields a high specific-binding-to-non-specific-binding ratio. Subsequent binding of biotinylated goat-anti-rabbit immunoglobulin (@alpha@RIgG-biotin) to (strept)avidin as a capture molecule allows the system to be used as an immunoassay for the target molecule, rabbit immunoglobulin (RIgG). Changing the ratios of PLL-g-PEG and PLL-g-PEG/PEGbiotin in the mixture changes the distribution of docking sites (biotin sites) on the interface and, thus, allows optimization of the sensing response. The effects of protein charge and the ionic strength of the buffer are also explored. We expect that such a platform could serve as a powerful tool for the investigation of molecular recognition effects.

10:40am **BI-MoM4 Self-Assembly of Modified Porphyrin Monolayers**, ***A.L. Bramblett**, M.S. Boeckl, K.D. Hauch, T. Sasaki,* University of Washington*; J.W. Rogers, Jr.,* Pacific Northwest National Laboratory*; B.D. Ratner,* University of Washington

Assembled monolayers can be used to deliver recognition signals to biological systems. Planar, multi-ring porphyrin structures can provide precision lateral control of chemistry at interfaces. Porphyrin molecules, which have peripheral constituents with the ability to hydrogen bond or coordinate to a metal, are predicted to form ordered molecular monolayers on gold surfaces in a side-by-side orientation. TPyP-Ge-Disulfide (a Ge coordinated pyridyl substituted porphyrin with two disulfide ligands) has been synthesized for use in self-assembling porphyrin monolayers, which form when one of two disulfide ligands binds to the gold surface. Self-assembled monolayers of TPyP-Ge-disulfide have been prepared on gold for characterization. X-ray photoelectron spectroscopy (XPS) of TPyP-Ge-disulfide shows that the atomic composition of the surface is consistent with a porphyrin monolayer, and approximately 50% of the sulfur atoms are bound to gold. Further, ultraviolet-visible spectroscopy (UV/Vis) shows a red shift in the peak of the Soret band, which is indicative of side-by-side porphyrin orientation when self-assembled. @footnote 1@ In addition, monolayers formed utilizing hydrogen bonding between the TPyP-Ge-disulfide and TCP (benzoic acid derivatized porphyrin), or utilizing Zn@super 2+@ coordination with the pyridyl nitrogen in TPyP-Ge-disulfide will be characterized using XPS, UV/Vis, and scanning tunneling microscopy, to examine the porphyrin arrangement on the gold surface. By chemically modifying the remaining free disulfide bond, these monolayers could be used to present biological ligands of interest in a spatially controlled manner. @FootnoteText@ @footnote 1@ Boeckl, M. S.; Bramblett, A. L.; Hauch, K. D., Sasaki, T.;Ratner, B. D.; Rogers, Jr, J. W. Langmuir 2000, 16, 5644-5653

11:00am **BI-MoM5 Efficient New Method of Nucleic Acid Immobilization**, ***Y. Wu**, P.L. Dolan, L.K. Ista, M.A. Nelson,* University of New Mexico*; R.L. Metzenberg,* Stanford University*; G.P. Lopez,* University of New Mexico

The field of DNA microarray technology has necessitated the cooperative efforts of interdisciplinary scientific teams to achieve its primary goal of rapidly measuring preferential gene expression in an organism. To that end, a collaborative effort to produce a chemically reactive surface on glass slide substrates to which DNA will covalently bind for use in and advancement of cDNA microarray technology was undertaken. We have developed a chemical process for covalently linking unmodified DNA to an ordinary microscope slide in a manner that preserves the ability of the immobilized nucleic acid to hybridize to complementary sequences. The method of binding DNA to solid surfaces considerably increased the consistency and uniformity of attachment, and reduced DNA loss during the experimental process when compared to other commonly used commercially available methods. Moreover, better hybridization results have been generated compared to commercially available immobilization techniques. In general, this method allows binding of single- and double-stranded nucleic acids onto a solid substrate that can lead to considerable improvements in hybridization of complementary sequences, stability of affixed DNA, and re-usability of microarrays. Following our immobilization process, arrayed slides were reusable for at least 5 times. In addition, the hybridization data has been analyzed quantitatively and successfully correlated with solution concentrations. Although this method is originally designed for forming DNA microarrays, it is likely also suitable for the immobilization of proteins, ribozymes and aptamers onto certain solid substrates..

11:20am **BI-MoM6 Probe Density Effects for Target Hybridization in DNA Monolayer Films Studied By SPR**, ***A.W. Peterson**, R.J. Heaton, L.K. Wolf,* Boston University*; R.M. Georgiadis,* Boston University, usa

Understanding probe to target interactions for surface immobilized duplexes is important in the emerging applications of DNA biosensors. We use in-situ surface plasmon resonance spectroscopy to monitor the kinetics of probe immobilization and target/probe hybridization for thiol-modified probes immobilized on gold. We find that both the efficiency and kinetics of probe/target hybridization depend strongly on probe density. Immobilization conditions can be used to control probe density and we investigate the effects of solution ionic strength, electrostatic potential at the interface and whether duplex or single stranded probes are immobilized. Independent of which immobilization strategy is used, we find that DNA films of equal probe density exhibit reproducible efficiencies and kinetics for probe/target hybridization. In addition, the hybridization isotherms show a distinct dependence on probe density. Insight into the mechanism of these probe/target interactions are investigated and discussed in the context of the observed kinetics.

11:40am **BI-MoM7 Two-dimensional Arrangements of Streptavidin on Biotin-doped Supported Lipid Bilayars Optimized for DNA-DNA Hybridization***, C. Larsson, E. Fridell, B. Kasemo,* ***F. Höök,*** Chalmers University of Technology, Sweden

In this work the quartz crystal microbalance with dissipation monitoring (QCM-D), surface plasmon resonance (SPR) and ATR-FTIR techniques were used to follow the 2-D arrangement of streptavidin on a biotinylated phospholipid bilayer supported on a SiO2 surface, for optimized capture of single stranded biotin-DNA (15- and 30-mer) and subsequently hybridization-kinetics measurement of their reaction with mixed-sequences of DNA (15- and 30-mer) with various degrees of mismatch. The QCM-D and ATR-FTIR data suggest that streptavidin rearranges into a more rigid and oriented structure at approximately 50 % coverage, interpreted as onset of crystallization. Interestingly, immobilization of biotin-DNA followed by subsequent hybridization prior to this stage results in up to a two-fold more rapid association kinetics compared with immobilization and hybridization at full coverage of streptavidin. Our results demonstrate how real-time control of the immobilization step can be efficiently used to minimize the influence from lateral interactions for surface-based biorecognition detection, and thus optimize hybridization kinetics measurements. The QCM-D data were also used to quantify variations in the viscoelastic properties of the formed layers of DNA and DNA duplexes, which were further correlated to the obtained results onhybridization kinetics.

Electrochemistry and Fluid-Solid Interfaces
Room 111 - Session EC-MoM

Surface Processes in Electrocatalysis

Moderator: E.M. Stuve, University of Washington

9:40am **EC-MoM1 Surface Science Studies of Model Fuel Cell Electrocatalysts***,* ***N. Markovic,*** Lawrence Berkeley National Laboratory **INVITED**

10:20am **EC-MoM3 The Surface Electrochemistry of Carbon Monoxide and Methanol on Solid Electrodes and Supported Catalysts***,* ***C. Korzeniewski****, D. Kardash-Richardson,* Texas Tech University

The electrochemical oxidation of methanol and related small molecules has been of special interest in relation to fuel cell research. With improvements in the design of fuel cells that operate on methanol and hydrogen gas, there has been a great deal of interest in the chemical steps involved in the oxidation of methanol and its by-products on metal electrodes. In recent years, we have approached the study of methanol oxidation pathways with the use of electrochemical and spectroscopic analysis techniques. Dissociative chemisorption leading to adsorbed carbon monoxide (CO) is probed with surface infrared spectroscopy, formaldehyde is quantified with fluorescence spectroscopy, and the conversion of adsorbed CO to carbon dioxide is investigated with linear sweep voltammetry and potential step techniques. This presentation will describe studies of methanol electrochemistry on Pt and Pt-Ru alloy solid electrodes and supported nanometer-scale catalysts. In situ infrared measurements between ambient and 85 @super o@C demonstrate methanol dissociative chemisorption is thermally activated on high Ru content bulk alloys. On solid Pt and Pt-Ru electrodes, formaldehyde can be an important by-product of methanol oxidation. However, under similar conditions the oxidation of methanol on nanometer-scale catalysts of Pt and Pt-Ru appears to be more complete. Attempts to correlate the properties of nanometer-scale metal particles and methanol oxidation pathways will be discussed.

10:40am **EC-MoM4 Measurement of Elevated Temperature Rate Processes Involved in Methanol Electro-Oxidation on Supported Platinum Catalysts***,* ***T.H. Madden****, E.M. Stuve,* University of Washington

Development of fuel cell catalysts for elevated temperature applications requires electrochemical techniques able to simulate these conditions. A dual electrolyte flow cell (DEFC) technique has been developed, capable of independent half-cell measurements of methanol oxidation and poisoning adlayer coverage in supported catalyst layers over a wide range of temperatures (25-100 °C) and pressures (0-2.5 atm gauge) at ~100% catalyst utilization while maintaining potential control at all times.@footnote 1@ Recent measurements indicate that increasing the temperature from 50 to 100 °C at 0.35 V@sub PdH@ results in substantial increase in methanol electro-oxidation rates with a ~70 kJ/mol activation energy yet only slight variation in the measured adlayer charge. Tafel slope and stripping charge results at 100 °C indicate the onset of significant CO electro-oxidation rates at 0.33 V@sub rhe@. High CO@sub 2@ yields measured at 100 °C and potentials less than 0.33 V@sub rhe@ indicate a possible role of CO thermal desorption or parallel-path oxidation. However, independent measurements of CO electro-oxidation, CO thermal desorption, and parallel-path oxidation are required to elucidate the respective role of these processes in elevated temperature methanol electro-oxidation. Results of such measurements will be presented for supported Pt catalysts using the DEFC technique augmented with pulsed reactant injection. @FootnoteText@ @footnote 1@ T.H. Madden and E.M. Stuve, submitted to J. Electrochem. Soc. (2001).

11:00am **EC-MoM5 Ruthenium, Osmium, and Palladium Modified Platinum Elecrodes: Surface Structure and Reactivity***,* ***A. Crown****, A. Wieckowski,* University of Illinois at Urbana-Champaign

We have used Scanning Tunneling Microscopy (STM) to examine spontaneously deposited ruthenium and osmium adlayers on the well-defined Pt(111), Pt(100), and Pt(110) electrodes.@footnote 1,2@ Clearly, ruthenium and osmium are deposited as arrays of surface islands, as in the case of ruthenium deposits obtained by electrolysis.@footnote 3@ Using STM, we have calculated ruthenium and osmium coverage values obtained by spontaneous deposition for various deposition times. The islands formed are mainly monoatomic--only a small fraction of the islands, depending on the Pt face, display a second monolayer deposit. Using in-situ STM, two-dimensional motions (or surface rearrangements) of highly structured islands of electrodeposited ruthenium, osmium, and palladium will be studied. The surface motions of platinum surface atoms, those of adsorbed carbon monoxide generated from methanol, and oxygen-containing species will also be investigated. We will attempt to address the surface mobility of the islands at various admetal coverage values. Examination, in situ, of the growth process will further elucidate the formation process, e.g., whether the islands tend to merge when the surface is exposed to a supporting electrolyte. Electrode potential will also be adjusted to examine the surface structure changes. The reactivity of these surfaces with respect to small organic compounds will also be examined. These experiments will lead us to the development of specific surface dynamics-reactivity relationships for the field of electrochemical surface science, with regards to surface poisoning phenomena and, in general, to electrocatalysis, including fuel cell catalysis. @FootnoteText@ @footnote 1@ Crown, A., Moraes, I.R.; Wieckowski, A.; J. Electroanal. Chem., 2001, 500, 333. @footnote 2@ Crown, A.; Wieckowski, A.; PCCP, in press. @footnote 3@ S. Cramm, K. A. Friedrich, K.-P. Geyzers, U. Stimming and R. Vogel, Fresenius J. Electroanal. Chem. 1997, 358, 189-192. .

Electronics
Room 130 - Session EL-MoM

Ferroelectric

Moderator: Y. Liang, Pacific Northwest National Laboratory

9:40am **EL-MoM1 Quantitative Analysis of Piezoresponse Force Microscopy: Electrostatic vs. Electromechanic Interactions***, S.V. Kalinin,* ***D.A. Bonnell****,* University of Pennsylvania

One of the critical aspects of the behavior of ferroelectric materials, both in the context of nano domains and for thin films, is the inter relation between atomic polarization and compensation charge. Piezoresponse force microscopy (PFM) has provided insight on domain structure and polarization reversal processes on the nanometer level. However, the imaging mechanism in PFM is complex in that both electrostatic and electromechanic interactions can contribute to image contrast. Here we analyze the electrostatic and electromechanical contrast in PFM using analytical solutions for the electrostatic sphere-dielectric plane problem coupled to Hertzian contact for the piezoelectric indentation problem. With this analysis local piezo electric properties can be quantified from traditional PFM and we suggest a novel variant that reduces the effects of system resonances to the contrast. The latter allows the measurement excitation and the domain switching bias to be decoupled. We use this approach on BaTiO@sub 3@ (100) to examine compensation charge and switching behavior.

10:20am **EL-MoM3 Template Sol-Gel Synthesis and Characterization of BaTiO@sub 3@ Nanostructures***, **B.A. Hernandez**, K.C. Chang, E.R. Fisher, P.K. Dorhout,* Colorado State University

Barium titanate in both its cubic and tetragonal form has shown relevance in many applications. A high dielectric constant, ferroelectric behavior, and electro-optical properties make this material a candidate for many applications in the microelectronics industry (e.g. capacitors and DRAMs). Recently, thin films and submicron size particles of BaTiO@sub 3@ have been studied and have shown that dielectric and ferroelectric properties change as a function of grain size and density of the particles. To explain these effects, Landau-Devonshire theory has been applied to both thin film and particle geometry. As far as we know, no one has studied size effects in high aspect ratio BaTiO@sub 3@ nanostructure materials. Thus we have developed a synthetic strategy to produce high aspect ratio nanostructures via a sol-gel template method. A chelate sol-gel solution was made using Ba(OAc)@sub 2@ and Ti(Opr@super i@)@sub 4@. Whattman Anodisc Membranes with a 200 nm pore size were dipped into the solution, allowed to air dry, and then calcined to the appropriate temperature for the tetragonal or cubic phase. SEM analysis shows that the structures can be thought of as fibers with a 200 nm diameter and 50µm length. Powder X-ray diffraction, Raman Spectroscopy, and Differential Scanning Calorimetry of the structures confirmed the production of cubic and tetragonal phases when fired at 700°C and 900°C respectively. Dielectric behavior and polarization data also will be presented.

10:40am **EL-MoM4 Low-temperature Process of (Y@sub 0.95@,Bi@sub 0.05@)MnO@sub 3@ Ferroelectric Thin Film and its Structural and Electrical Properties***, **T.J. Choi**, Y.S. Kim, J. Lee,* Sung Kyun Kwan University, Korea

(Y@sub 0.95@,Bi@sub 0.05@)MnO@sub 3@ (YBM) on Pt and Y@sub 2@O@sub 3@ buffered Si (100) have been prepared by pulsed laser deposition. Addition of Bi in YMnO@sub 3@ enhanced crystallization of YMnO@sub 3@ thin films. The c-axis oriented YBM films have been obtained on Pt and Y@sub 2@O@sub 3@/Si at 700 °C, which is lower deposition temperature than that of typical YMnO@sub 3@ films. The processing conditions of depositing oxygen partial pressure and cooling atmosphere have affected crystallization behavior and electrical properties of YBM films. At low oxygen partial pressures, (111), (112) and c-axis oriented polycrystalline nature were observed. As the oxygen pressure increased, YBM films intended to grow with c-axis preferred orientation. YBM deposited in oxygen pressure of 100 mTorr was strongly oriented along the c-axis at the substrate temperature of 700 °C. YBM grown on Y@sub 2@O@sub 3@/Si had a hysteresis curve with a clockwise direction, which indicates that the C-V hysteresis curve is caused by ferroelectric polarization switching. The memory window was about 2 V at a sweep voltage of 8 V.

11:00am **EL-MoM5 Effects of Bi/Sr Stoichiometric Ratio on Electrical Properties of Pt/SrBi@sub 2@Nb@sub 2@O@sub 9@/Si Ferroelectric Gate Structure***, **Y.T. Kim**, S.I. Kim,* Korea Institute of Science and Technology, Korea*; I.H. Choi, H.S. Choi,* Korea University, Korea*; C.W. Lee,* Kookmin University, Korea

In comparison with high dielectric constant (k) isotropic ferroelectric materials such as Pb(Zr,Ti)O@sub 3@ (PZT), and PLZT for the storage capacitor, Bi-layered perovskite materials have relatively low k and some advantages such as excellent fatigue resistance, low leakage current. Especially, for MFSFETs, SrBi@sub 2@Nb@sub 2@O@sub 9@ (SBN) seems to be a promising candidate among the Bi-layered perovskite family because it has relatively lower k than SBT.@footnote 1@ It is well known that the lower k, the higher electric field is applied to the ferroelectric thin film.@footnote 2@ The high electric field causes greater memory window, which becomes now an issue for the application of MFSFETs as cell devices in the non destructive readout ferroelectric random access memory (NDRO-FRAM) with low voltage operation. In this work, in order to control the Bi/Sr stoichiometric ratio, we used SrNb@sub 2@O@sub 7@ and Bi@sub 2@O@sub 3@ targets with different powers of rf magnetrons. As a result, we have found that electrical properties are strongly sensitive to the Bi content. The capacitance-voltage (C-V) characteristics and memory windows of Pt/SBN/Si gate were investigated with various Bi/Sr content ratios. The memory window of the Pt/SBN/Si gate with the Bi/Sr ratio of 3.1 becomes 1.8 V at applied voltage of 3 V, which is the greatest memory window so far. However, the memory window gradually increases with increasing the Bi/Sr ratio in the SBN thin films, but when the Bi/Sr ratio becomes over than 3.1 the electrical properties such as memory window and breakdown voltage becomes to be degraded. The SBN thin film with Bi/Sr ratio of 3.1 has the (008) preferred orientation after annealing at 600°C for 1hr in O@sub 2@ ambient, which is relatively lower recrystallization temperature than that of other Bi-layered perovskite family. Particularly, in order to improve the memory window, it has been used to insert buffer insulators such as CeO@sub 2@, Y@sub 2@O@sub 3@, and YMnO@sub 3@,2). However, in this work, we can obtain the greatest memory window without a buffer insulator. @FootnoteText@ @footnote 1@ Y. T. Kim and D. S. Shin, Appl. Phys. Lett. 71, 3507 (1997) @footnote 2@ H. N. Lee, Y. T. Kim and Y. K. Park, Appl. Phys. Lett. 74, 3887 (1999)

11:20am **EL-MoM6 Recent Progress of Ferroelectric Memory Materials and FET-type FeRAMs***, **H. Ishiwara**,* Tokyo Institute of Technology, Japan **INVITED**

A new class of ferroelectric materials was synthesized by adding sol-gel solution of a dielectric material to that of conventional ferroelectric materials such as PbZr@sub 1-X@Ti@sub X@O@sub 3@, SrBi@sub 2@Ta@sub 2@O@sub 9@, and Bi@sub 4@Ti@sub 3@O@sub 12@. It was found that the crystallization temperature of the new materials was decreased by 150°C to 200°C compared to the original materials and that the surface of the crystallized film was extremely flat. It was also found that the ferroelectric properties were almost the same as or even better than the original ones. Thus, a 13-nm-thick Bi@sub 4@Ti@sub 3@O@sub 12@-based film with a saturation polarization voltage of 0.5 V was obtained. Concerning the FET-type FeRAMs (ferroelectric random access memories), improvement of the data retention characteristics is most important. To improve the retention time, the buffer layer material, which was necessary to insert between the ferroelectric gate film and a Si substrate for preventing interdiffusion of the constituent elements, was optimized, as well as the structure of the ferroelectric-gate FET was carefully designed. As a result, MFIS (metal-ferroelectric-insulator-semiconductor) diodes with excellent characteristics were fabricated by combination of a Si@sub 3@N@sub 4@ buffer layer and a c-axis-oriented Bi@sub 4@Ti@sub 3@O@sub 12@ film. In order to further improve the retention characteristics, a prototype of the 1T2C cell was also fabricated, in which two ferroelectric capacitors with the same area were connected to the gate terminal of an MOSFET so that the depolarization field was not generated. In this cell, nondestructive readout operation up to 10@super 4@ times and the excellent data retention up to 17 hours were realized.

Magnetic Interfaces and Nanostructures
Room 110 - Session MI+EL-MoM

Magnetic Devices

Moderator: B.A. Everitt, Seagate Technology

9:40am **MI+EL-MoM1 High Speed 256k Magnetoresistive RAM***, **S. Tehrani**,* Motorola Corporate **INVITED**

Magnetoresistive Random Access Memory (MRAM) has the potential to be a high-speed, low-voltage, high-density, nonvolatile solid state memory. MRAM is based on magnetic memory elements integrated in a backend process with standard CMOS semiconductor circuitry. Key attributes of MRAM technology are nonvolatility and unlimited read/write endurance. Our bit architecture is based on a minimum-sized active transistor as the isolation device in conjunction with a magnetic tunnel junction element (MTJ) defining the MRAM bit. Our MTJ material stack is composed of two magnetic layers separated by a thin dielectric barrier with the polarization of one of the magnetic layers pinned in a fixed direction. The resistance of the memory bit is either low or high dependent on the relative polarization, parallel or anti-parallel, of the free layer with respect to the pinned layer. In this talk we will summarize our progress on MRAM based on MTJ integrated with CMOS circuitry. We have demonstrated MTJ material in the 10 kOhms-um^2 range with MR values up to 50 %. The MRAM module is inserted in the back-end-of-line (BEOL) interconnect using four additional lithography steps. The source and isolation are shared between neighboring cells to minimize cell area. In this particular architecture, the cell size is 7.2um^2, corresponding to 9f^2, where f is one-half the metal pitch. We have developed a 256kb (16k x 16) MRAM memory based on 0.6 um CMOS with a 1T1MTJ (one transistor and one MTJ) cell. Nonvolatile data storage and read cycle times of 35 ns have been demonstrated. Read power consumption at 3.0V and 20MHz is about 24mW. These results show that MRAM based on MTJ has the potential to be a competitive memory with the attributes of high-speed read and write, as well as nonvolatility. The progress, potential and challenges of MRAM technology will be discussed. @FootnoteText@ This work in funded in part by DARPA.

10:20am **MI+EL-MoM3 Dry Etching of MRAM Device Structures***, **R.A. Ditizio**, G. Beique,* Tegal Corporation

Magnetic Random Access memory (MRAM) has experienced a rise in interest in recent years as an alternative to other non-volatile memory devices. As efforts continue to improve the electrical performance of these devices, parallel efforts are underway to meet the stringent requirements for the fabrication of MRAM device structures at high densities. In this report, recent efforts that have been undertaken to apply conventional etch practices to the unique requirements for the patterning of MRAM device structures in an inductively coupled plasma source are discussed. In particular, improvements in optical emission detection and the subsequent correlation of endpoint traces to films in the device structure will be presented. Correlation of the film structure to the optical emission trace is necessary, for example, as a means to identify the specific time in the etch process at which to stop on the thin insulating layer across which a magnetic tunneling junction might typically be formed. Post-etch corrosion control of the completed device structure using an integrated rinse module is also discussed.

10:40am **MI+EL-MoM4 Spin Dependent Tunneling Devices for Nonvolatile Latch Memory***, **M. Tondra**, D. Wang, D.J. Brownell, Z. Qian, C. Nordman, J. Daughton,* NVE Corp. **INVITED**

Operation of integrated magnetoresistive nonvolatile latch cell memory using spin dependent tunneling (SDT) junctions has been demonstrated. These SDT devices were fabricated on top of commercially processed CMOS silicon circuit wafers. Fabrication of these devices presents many challenges to thin film deposition process developers. Process temperature compatibility and surface roughness are prime examples. In spite of these and other technical challenges, there is significant motivation to continue developing SDT fabrication processes. In particular, SDT devices provide resistance changes on the order of 50% (large signal), a wide range of resistance values (for low power applications), and magnetic switching speeds beyond 1 GHz. Furthermore, the SDT cell density is potentially competitive with commercial SRAM and DRAM. Recent success in SDT integrated device fabrication has been a result of using new approaches to surface preparation. Specifically, chemical mechanical polishing (CMP) has been employed to create a sufficiently smooth surface for SDT deposition. In-process atomic force microscopy (AFM) measurements suggest that a pre-deposition RMS substrate roughness of 0.2 nm is sufficient to allow successful SDT fabrication. This paper will discuss device-specific process details of SDT latch cells and their impact on the potential for near-term commercialization.

11:20am **MI+EL-MoM6 Effects of Interfacial Electronic States and Roughness on Tunnel Magnetoresistance***, **J. Inoue**, H. Itoh,* Nagoya University, Japan

Recently, active researches on tunnel magnetoresistance (TMR) are under progress with the objects of its technical applications such as magnetic sensors and magnetic random access memories. In spite of these studies, the understanding of the electronic states at the interfaces of the ferromagnetic tunnel junctions and of the effects of roughness on the tunnel conductance and TMR is not still complete. Quite recently, numerical results on the TMR in the first principles band calculations have been reported for junctions with clean interfaces. The calculated results show that the contribution of the states with certain wave vectors parallel to the interface becomes dominant, which are known as hot spots. We calculate the dependence of the tunnel conductance and TMR on the barrier thickness including the interface roughness, and show that the contribution of the hot spots to the tunnel conductance is reduced by the roughness. We further argue the possibility of appearance of interfacial state due to amorphous-like barrier structure and its effects on the TMR.

11:40am **MI+EL-MoM7 Performance of the BARC Magnetoresistive Sensor****, **J.C. Rife**, R.J. Colton, M. Miller,* Naval Research Laboratory*; M.A. Piani,* Nova Research, Inc.*; C.R. Tamanaha,* Geo-Centers, Inc.*; P.E. Sheehan, L.J. Whitman,* Naval Research Laboratory

The Bead ARray Counter (BARC) is a microfabricated chip for quantitatively detecting and identifying biological molecules using giant magnetoresistive (GMR) sensors.@footnote 1@ The assay is based on highly selective biomolecular binding to the surfaces of numerous individually addressable GMR sensors, followed by labeling of captured molecules with magnetic beads. An externally applied AC magnetic field magnetizes the beads and a lock-in amplifier detects changes of 10@super -@@super 7@ in resistance of the GMR sensors, limited by Johnson and 1/f noise. Overall sensitivity is a convolution of chemical and magnetic/electronic sensitivities. Our current sensors can determine target concentrations from 10 fM to 1 nM with loading of one hundred to more than a thousand beads. In principle, each sensor could detect one bead/one captured molecule. Present electronic sensitivity is restricted, in part, by the properties of the commercial 2.8 µm diameter composite polymer/ferrimagnetic beads that result in signal levels a factor of ten below the electronic noise floor. We find 10 to 100x improved signal with solid, soft ferromagnetic beads of the same size that yield the theoretical susceptibility of solid magnetic spheres, but chemical functionalization of the surfaces is not yet resolved. We have measured bead signals versus magnetizing field to have an approximately square-law dependence determined by the magnetoresistance response curve. We have also measured the bead signal versus position across the 2 µm wide GMR sensor and generated a simple model of the local resistivity change. Finally, We have developed an overall model for the GMR sensor response that agrees in large part with the measurements. The model should enable sensor and magnetic physical design to be optimized for maximal chemical and electronic sensitivity. *Supported by the Defense Advanced Research Projects Agency. @FootnoteText@ @footnote 1@ Edelstein et al., Biosensors & Bioelectronics 14, 805 (2000).

Manufacturing Science and Technology
Room 131 - Session MS-MoM
Metrology and Inspection for Manufacturing

Moderator: C.R. Brundle, Applied Materials

9:40am **MS-MoM1 Optical Digital Profiling for Production Applications***, **K. Barry**, J. Kretzschmar, N. Jakatdar,* Timbre Technologies, Inc. **INVITED**

As the industry drives down feature sizes, the need for more advanced characterization techniques becomes imperative. Gate lengths are quickly approaching the sub-one hundred-nanometer regime. Traditional techniques are not keeping pace with the precision and accuracy needs of the IC industry. Additionally, with the onset of 300mm wafer production, it will be imperative for tools to be able to measure critical parameters and adjust processing conditions on a wafer-by-wafer basis. The industry is experiencing a paradigm shift in critical dimension metrology. Optical Digital Profilometry (ODP), developed by Timbre Technologies Inc. (Fremont, Calif.), is an optical, nondestructive, in-line profile measurement methodology utilizing Maxwell's principles to generate digital cross-sectional representations of IC features. One advantage is that ODP has been proven extendible beyond the 70nm node by utilizing spectroscopic ellipsometry to measure physical structures with precision an order of magnitude better than currently available CD-SEMs. Another advantage lies in Optical Digital Profilometry's ability to generate digital cross-sectional information in real time enabling advanced process control (APC) of IC manufacturing lines. In this paper we present results from monitoring production wafers via ODP of shallow trench isolation (STI) structures at the post-etch, post-clean step, also referred to as final inspect (FI). These results show ODP to be a viable method for in-line CD, depth, and profile metrology, with sub-nm repeatability and excellent correlation to XSEM and CD-SEM.

10:20am **MS-MoM3 Critical Dimension and Profile Measurement by Optical Scatterometry for Sub-0.15 µm Advanced Gate and Shallow Trench Isolation Structures***, **D. Mui**, H. Sasano, J. Yamatino, M.S. Barnes, K. Fairbarn,* Applied Materials

The use of a non-destructive optical scatterometry (OS) technique for measuring critical dimensions (CD) and cross-sectional profiles in advanced gate and shallow trench isolation (STI) structures with sub-0.15 µm feature size has been evaluated. Conventional scanning electron microscopy (SEM) technique was used as the reference for comparison. 8" Si wafers with various feature sizes and profiles were used in this study. A bias between optical-CD (OCD) and SEM-CD measured on the same feature was observed. Measurements on different OS tools from different vendors showed consistently smaller CDs than those measured on a SEM tool. This CD bias was observed to be profile dependent ranging from 2 to 20 nm in our study. Good correlation between the two CD metrologies was obtained for a given wafer when a constant bias was added to the OCD data set. For profile comparison, various profiles including - bowed, tapered, notched, and vertical, were etched and measured. In general, good correlation was obtained between the non-destructive OS and destructive SEM techniques.

10:40am **MS-MoM4 Wafer Inspection with HDI Surface Reflectance Analyzer***, **A. Surdutovich**, G. Conti, H.T. Nguyen, H. Hao,* Applied Materials*; G.H. Vurens,* HDI Instrumentation

Scanning Reflectance Analysis (SRA) is being widely used in the hard disk industry for metrology of thin film disks. The technique has been evaluated for wafer inspection. This technique provides a means to generate high resolution maps of thickness variation and empirical chemistry variation of films on a wafer in less than one minute. Low k CVD films have been measured with HDI SRA and an application has been developed for mapping out separately chemical and thickness variations across the whole wafer area. Detection of organic contamination on Cu seed film has also been investigated.

11:00am **MS-MoM5 Using SQUIDs for Failure Analysis in the Semiconductor Industry***, T. Venkatesan, L.A. Knauss, **A. Schwartz**,* Neocera, Inc. **INVITED**

With the arrival of flip-chip packaging and multi-level metallization on dies, present tools and techniques are having increasing difficulty in meeting failure analysis needs. Recently a magnetic field imaging system has been demonstrated to localize shorts in buried layers of both packages and dies. This system uses a SQUID (Superconducting Quantum Interference Device), which is a very sensitive magnetic sensor that can image magnetic fields generated by magnetic materials or currents (such as those in an integrated circuit or package). These currents (as low as microamperes) can be detected even when they are buried deep within a package or assembly. Since magnetic fields are not affected by most materials used in circuit technology, magnetic field imaging can be applied to several vertical layers enabling problem detection in a multi-layer stack involving the die, solder bumps, package, BGA and board. The current density distribution in the sample can then be calculated from the magnetic field image providing a map of current flow in the assembled device. This can be helpful for design verification and short localization, including determining which layer of the structure contains the defect. To image these devices, the SQUID must be cooled to temperatures around 77K while the sample is at room temperature. In order to image these parts non-invasively, the system has been designed to keep the SQUID cold and in vacuum while the sample is at room temperature in air. The design of this system as well as the application to failure analysis will be presented. Peak localization of defects to ± 5 microns has been demonstrated in the best case with sub-10 microns being typical.

11:40am **MS-MoM7 Development of a 300 mm Wafer Defect Analysis Tool Integrating High Resolution Auger Spectroscopy and Ultrahigh Resolution Immersion Lens SEM Microscopy***, **W.K. Ford**, M. Jaehnig, P. Hudson,* Intel Corporation*; T. Dingle, K. Troost, L. Christman, J. Jackman, M. Verheijen,* FEI Company*; P. Belcher,* Thermo VG Scientific

The challenge of defect analysis and material characterization in a Si semiconductor fab becomes increasingly difficult with each process generation. Scaling steadily decreases the size of circuit features, permitting smaller and smaller particle defects to impact the yield of the device. Simultaneously, nanometer-scale thin films are commonly being used as gate dielectrics, metal adhesion and barrier layers, and interfacial treatments. These two trends produce challenges to process development and manufacturing that can be addressed using surface analytical tools such as the Auger microscope. This paper describes the development of an advanced Auger microscope believed suitable for 0.13 µm, 0.10 µm, and 0.07 µm process generations. It is in this range that the large excitation volume of the electron beam even at the lowest practical primary beam energy renders as ambiguous the commonly used x-ray analysis (EDS) methods, and that ultra sensitive mass spectroscopy (TOFSIMS) fails to have suitable lateral spatial resolution. The Auger microscope described herein has been developed using an immersion mode objective lens for ultimate imaging capability, providing simple, rapid transition between ultra high resolution SEM imaging and Auger spectroscopy. It is based on a UHV 300 mm wafer-capable platform using industry standard interfaces and incorporates a new, highly effective stage technology, which provides for the required stage navigation accuracy and speed, versatile sample positioning including high angle tilting, and full integration with standard CAD software interfaces. A high sensitivity Auger detector is used that provides the high spectral energy resolution often required for chemical analysis. These capabilities will be demonstrated using a full range of examples derived from Si process development and manufacturing.

Processing at the Nanoscale
Room 133 - Session PN-MoM

Atomic/Nano-scale Manipulation

Moderator: J. Murday, Naval Research Laboratory

9:40am **PN-MoM1 The "Millipede" - More than 1000 Tips for parallel and dense AFM Data Storage***, P. Vettiger, G. Cross, M. Despont, U. Drechsler, U. Dürig, W. Häberle, M.I. Lutwyche, H.E. Rothuizen, R. Stutz, R. Widmer, G.K. Binnig,* IBM Research, Zurich Research Laboratory, Switzerland*; **T. Albrecht**,* IBM Almaden Research Center **INVITED**

A MEMS-based AFM-array concept ("Millipede") for data storage of potentially ultrahigh density, terabit capacity, and high data rate is presented. Its storage potential has been demonstrated by a new thermomechanical local-probe technique to store, read-back and erase data in very thin polymer films. With this new technique, 30- to 40-nm-sized bit indentations of similar pitch size were made by a single cantilever/tip in a 50-nm-thin PMMA layer, resulting in a data storage density of 400-500 Gb/in.@super 2@. High data rates are achieved by parallel operation of large 2D AFM arrays batch-fabricated by silicon surface-micromachining techniques. The VLSI of micro/nanomechanical devices (cantilevers/tips) on a single chip leads to the largest and densest 2D array of 32x32 (1024) AFM cantilevers with integrated write/read storage functionality ever built. Time-multiplexed electronics control the write/read storage cycles for parallel operation of the Millipede array chip. Initial areal densities of 100-200 Gb/in.@super 2@ have been achieved with the 32x32 array chip, which has potential for further improvements.@footnote 1@ This constitutes a major step towards future ultra-dense data storage with potential capacities beyond today's storage approaches. The Millipede concept focuses on a polymer storage media, but may be expanded to other media, and not excluding magnetics, provided suitable read/write functionality can be integrated into cantilevers and tips. We also envision that Millipede may open up new perspectives in nanoscale science and technology areas such as lithography, high-speed/large-scale imaging, molecular and atomic manipulation, biotechnology and many others. @FootnoteText@ @footnote 1@P. Vettiger et al., IBM J. Res. Develop. 44, 323 (2000); M. I. Lutwyche et al., Appl. Phys. Lett. 77, 3299 (2000).

10:20am **PN-MoM3 Attractive Mode Manipulation of Fullerenes on Si(100)***, **D.L. Keeling**, M.J. Humphry, P.H. Beton, P. Moriarty, M.A. Phillips,* University of Nottingham, UK

Room temperature STM manipulation of C60 on silicon surfaces under ultra-high vacuum has been investigated. A new intrinsic attractive mode of manipulation has been observed for gap impedances 1-3GOhm in which molecules hop towards the tip in steps of 1-3 lattice constants. These effects are observed in both polarities although a greater stability and higher probability for attractive mode manipulation is observed for negative sample bias. A similar effect can give rise to a continuous dragging of the molecule while scanning, for which the displacement is parallel to the dimer rows. For lower gap impedance, ~1GOhm, repulsive manipulation, characterised by a sawtooth response of the tip similar to that reported by Bartels et.al., is observed in which the molecule is displaced across the surface in regular steps of 1 or 3 surface lattice constants. The response of molecules to manipulation is discussed in terms of a simple model for C60-Si(100) bonding in which two out of four Si-C bonds are broken during the manipulation process and a change in molecular orientation accompanies tip induced displacement.

10:40am **PN-MoM4 Reliable Nanofabrication Method on Au Cluster Films in a Non-contact Mode with an Atomic Force Microscope***, **K.-H. Park**, J.Y. Kim, J.S. Ha, K.-B. Song,* ETRI, Republic of Korea

Many kinds of nanofabrication methods have been studied on metal films using scanning probe microscopy so far. However, they are still far from the practical application for the data storage or lithography. Scanning tunneling microscopy(STM) is not an adequate technique because it reliably operates only at ultra high vacuum (UHV) and the throughput is very low.@footnote 1@ Contact mode fabrication methods of atomic force microscopy (AFM) also have shortcomings because the mechanical contact between the tip and the samples induces a significant damage to the tip apex causing the serious tip wear. Here, we devised a new reliable fabrication method by applying a local field on granular Au nanocluster films using conducting AFM tips in a noncontact mode. Au cluster thin films (10-50 nm) were deposited on silicons and glass substrates through the gas evaporation process under the partial Ar pressure of several mbar. The granular morphologies of the films are observed by STM at UHV in situ, and then the samples were transferred to an air ambient stage for AFM analysis. A reproducible creation of Au bits was obtained with the lateral dimension of 100 nm on granular films. The critical voltage for the fabrication is much larger than the case in a contact mode with some variation depending on the conductivity of the films. The reliability of nanofabrication is attributed to the field induced migration and current induced sintering mechanism without the contact process between the tip and samples. The near-field optical properties of fabricated structures are investigated in a view of an optical data storage. @FootnoteText@ @footnote 1@ K.-H. Park et al., Appl. Phys. Lett. v75, 139 (1999)

11:00am **PN-MoM5 Creating Nanoscale Patterns by Arranging Gold Nanocolloids with an AFM***, **S. Hsieh**, S. Meltzer,* University of Southern California*; C.R.C. Wang,* National Chung Cheng University, Taiwan*; A.A.G. Requicha, B.E. Koel,* University of Southern California

Combining lithography methods and controlled positioning and manipulation of nanosized building blocks is a promising technique for building future nanoscale devices, e.g., SETs or near-field photonic waveguides. Gold colloids can be fabricated in well-defined shapes and sizes and are therefore ideal components for such devices. We extended the capabilities demonstrated in this field by demonstrating the manipulation of Au nanorods and spherical particles by utilizing atomic force microscopy (AFM). For anchoring of Au nanorods and subsequent manipulation, the choice of adhesive layer is crucial. 3-Mercaptopropylmethyldimeoxysilane (MPMDMS) self- assembled layers adhere to the colloid particles and still allow their lateral manipulation. The colloids can be pushed by exerting a controlled lateral force on the particles with an AFM tip. Off-center pushing results in rotation of the nanorods. The parameters for successful manipulation of nanorods and spherical particles will be compared. These techniques for arranging nanoparticles and nanorods should be useful for fabricating new nanostructures or incorporating such nanoparticles into pre-fabricated structures.

11:20am **PN-MoM6 Dynamics and Manipulation of Surface Electronic States***, **R. Berndt**,* University of Kiel, Germany **INVITED**

We discuss two recent applications of scanning tunneling spectroscopy of surface electronic states. First, a long standing discrepancy between experimental and theoretical values for the lifetimes of holes in the surface state electron bands on noble metal surfaces is resolved with both found to have been in error. The ability of the scanning tunneling microscope to verify surface quality before taking spectroscopic measurements is exploited to remove the effects of defect scattering on experimental lifetimes. A theoretical treatment of inelastic electron-electron scattering is developed which explicitly includes intra-band transitions within the surface state band. In our model two-dimensional decay channels dominate the electron-electron interactions that contribute to the hole decay, screened by the electron states of the underlying three-dimensional electron system. Second, from a single Mn adsorbate placed within a geometrical array of adatoms on Ag(111) modification of the electronic structure is observed. The changes result from coupling between the adsorbate level and surface electronic states of the substrate. These surface states are scattered coherently within the adatom array, mediating the presence and shape of the array to the adsorbate within. The dimension and geometry of the adatom array thus provide a degree of control over the induced changes.

Plasma Science
Room 103 - Session PS1+MM-MoM
Science & Technology of Microplasmas and MEMS Processing

Moderator: M.G. Blain, Sandia National Laboratories

9:40am **PS1+MM-MoM1 The Challenges of Plasma Etching in MEMs Processing***, **G.R. Bogart**, J.T.C. Lee, A. Kornblit, H.T. Soh, K.E. Teffeau, F.P. Klemens, J.F. Miner,* Agere Systems **INVITED**

The rapid advancement in semiconductor technology has allowed for the design and manufacture of more complex microelectromechanical systems (MEMs). Tiny gears and simple microchannels have yielded to more complex integrated systems on a single chip. The applications of this new technology span multiple disciplines and accounts for the wider acceptance of these systems in the market place. While there are numerous methods to generate these micromachines, dry etching provides a level of manufacturing control that wet etching cannot deliver. Additionally, processes that were once limited to wet etching are now being asked of dry etching due to the added control. As an example, large ultra-thin membrane generation, while generally limited to wet etch processes, is now a possibility using dry etching techniques. For optical telecommunications components, the use of thin, silicon on insulator (SOI) wafers allows one to easily combine bulk micromachining with surface micromachining to generate well supported free standing structures. The new requirements that are being placed on dry etching processes have created issues that need to be handled in creative ways. Increasing aspect ratios with 90 degree sidewall angle specifications are competing against demands for higher etch rates, uniformity, selectivity, and other processing metrics. This paper will address some of the challenges that lie ahead for dry etching in the MEMs area.

10:20am **PS1+MM-MoM3 Maskless Etching of Silicon using Patterned Microdischarges**, *K.P. Giapis,* California Institute of Technology, U. S. A.*; **M. Sankaran**,* California Institute of Technology

Hollow cathode microdischarges have gained recent attention for their high-pressure operation and intense UV radiation. Due to their non-Maxwellian electron energy characteristics, they are capable of producing excited states such as excimers and radicals. For this reason, these discharges could serve as a source of reactive species for materials applications. In this talk, we will present the operation of CF4/Ar microdischarges and their potential use in silicon etching. Because of the ability to form discharges in small holes and lines, we have used devices as stencil masks to transfer patterns directly into bare substrates. Devices employed were fabricated in copper-polyimide structures with hole diameters of 200 µm. Discharges in flowing gas mixtures (25 sccm CF4 / 75 sccm Ar) were operated at 20 Torr with DC voltages less than 400 V and currents between 0.01-1 mA. Optical emission spectroscopy was used to detect the presence of etchants such as fluorine radicals. To etch n-type silicon (100), the 2-layer structure was patterned and pressed against the substrate. With the silicon as the cathode of the device, etch rates were found to be larger than 7 µm/min. SEM images showed profiles with a peculiar shape attributed to the expansion of the plasma into the etched void. The plasma expansion was also monitored by I-V characteristics which showed an approximate linear increase in discharge current during the etch time. This technique has also been applied to etching arrays of multiple holes and lines with similar resulting etch rates and profiles. Maskless pattern transfer in this dimensional range presents an alternative to laser drilling and ultrasonic milling.

10:40am **PS1+MM-MoM4 Efficiency of Microfabricated ICP Sources@footnote 1@***, **F. Iza**, J.A. Hopwood,* Northeastern University

Recently a micromachined 5 mm-inductively coupled plasma (ICP) source and its use in optical spectroscopy have been reported.@footnote 2,3@ The performance of this device in terms of ion density and power efficiency was poorer than expected in comparison with larger ICP systems. A simple model for micro-ICP sources suggested that increasing the frequency of operation and the coupling between the source and the plasma could lead to improved performance. New microfabricated devices operating at higher frequencies (690 MHz-818 MHz) and with improved coupling coefficients have been fabricated and characterized. Argon plasmas have been generated between 100 mtorr and 12 torr and have been sustained with as little as ~100mW. Probe measurements have been carried out to determine the ion density and electron temperature versus coupling coefficient, frequency, pressure and power. The electron temperature increases from 3 eV to 4.5 eV as the pressure decreases from 0.4 to 0.1 torr (53.3~13.3 Pa) independently of the frequency of operation and power absorbed by the device. Improved coupling coefficients lead to ion densities of 9x10@super 10@ cm@super -3@ at 400 mtorr while consuming only 1W. This ion density is three times larger than in previous micro-ICP sources under the same conditions. Increasing the frequency from 690 MHz to 818 MHz, however, does not increase the efficiency as predicted by previous models. A new model that incorporates the power dependence of the plasma resistance will be presented to explain this behavior. @FootnoteText@ @footnote 1@This work is supported by the NSF under Grant No. DMI-0078406. @footnote 2@J.Hopwood, O. Minayeva, and Y. Yin, "Fabrication and characterization of a micromachined 5 mm inductively coupled plasma generator", J. Vac. Sci. B 18, 2446, (2000). @footnote 3@O. Minayeva, and J.A. Hopwood, "Optical Emission Study of a Microfabricated Inductively Coupled Plasma", AVS 47th International Symposium, Paper MM-WeM4.

11:00am **PS1+MM-MoM5 Microhollow Cathode Discharge Flow and Stability***, **D.D. Hsu**, M.A. Nierode, D.B. Graves,* University of California, Berkeley

The microhollow cathode (MHC) is a geometry used to sustain atmospheric-pressure glow discharges. Flowing gas through an array of MHCs could be used to process surfaces. For example, nitrogen gas can be flowed through a microhollow cathode discharge (MHCD) in order to incorporate nitrogen onto a polymer, such as polyethylene terephthalate. Convective gas flow through the MHCD is found to affect the stability of these discharges. For example, helium flow greater than 300 sccm through a 200 µm hole at atmospheric pressure allows the MHCD to be sustained at a lower power than a stagnant helium discharge. In addition, the neutral temperature, measured by optical emission spectroscopy, of a helium-nitrogen discharge decreases when going from a stagnant discharge to one with gas flow. Higher flowrates of nitrogen through the hole cause the current to transition from a direct current to a pulsing current. The pressure drop across the hole and the gas flowrate suggest that Poiseuille flow can be used to model flow through an MHC. With pressure, peak temperature, and power deposition data, a fluid model of the discharge can help determine the spatial extent and temperature profile of the discharge. We will discuss the stability limits of these microplasmas as a function of power, pressure, gas flow, and gas composition.

11:20am **PS1+MM-MoM6 Experimental and Numerical Model Investigations of Miniature Microwave Plasma Sources***, D. Story, T.A. Grotjohn, **J.A. Asmussen**,* Michigan State University

In the past, the challenge in microwave plasma research was to develop techniques that provide high ion and free radical densities uniformly, over large and ever increasing process areas. Since scale-up was usually an important issue when considering industrial applications, the study of very small microwave plasmas, on the order of a few millimeters, was rarely done. Recently, interest in the development of systems on a chip, MEMS and their related micro system applications, has suggested the possibility of numerous applications for mini and micro plasma sources. Accordingly, this investigation is devoted to the development and the understanding of the behavior of very small microwave plasma sources. We have constructed two microwave plasma systems that create and allow for the experimental investigation of millimeter size plasmas. Plasma are generated across a wide range of input parameters, including pressure variation from below 1 Torr to 1 atmosphere, input power at 2.45 GHz from one watt to 100 watts, and a variety of gas mixtures including argon, nitrogen and hydrogen. Microwave plasma of various sizes (volumes) and aspect ratios are studied. Plasma density, size, shape, ignition, and emission spectra are monitored during each experiment to characterize the miniature plasma over the operating range. Companion global model and two dimensional numerical models will be developed and used to further understand the operation of miniature microwave plasma sources. The experimental and modeling results will identify the experimental operating regime necessary to excite and maintain stable, high density, miniature microwave plasma sources and will also identify the important figures of performance, such as electron temperature versus pressure/power and absorbed power densities versus pressure and plasma size.

11:40am **PS1+MM-MoM7 Potential and Current Profiles of Nitrogen Gas DC Microplasmas***, **C.G. Wilson**, Y.B. Gianchandani, A.E. Wendt,* University of Wisconsin-Madison

We have recently reported on@footnote 1@ DC microplasmas which have been generated between patterned thin-film metal electrodes on the surface of a wafer. Typical operating pressure and power density are in the range of 1-20 Torr and 1-10 W/cm@super 2@, respectively. The plasma extent can be varied from 1 cm by variations in the electrode area, operating pressure and power. Silicon etch rates of 4-17 µm/min have been achieved. This technology allows multiple independent etching microplasmas to be operated on a single silicon wafer, enabling parallel or consecutive processing. Applications for this include trimming of electronic and micromechanical components, ranging from resistors to resonant gyroscopes. In this paper we will report on characteristics of microplasmas generated by co-planar in-situ electrodes. Breakdown voltage has been found to differ from the Paschen curve, being more uniform over a wider range of pressures. Contour plots of the floating potential of microplasmas have been measured, and the bulk of the voltage drop in the plasma column has been found to be proximate to the cathode. The floating potential is non-uniform at equal heights over the cathode and is lowest close to the center of the electrode. The height of the plasma column is found to scale with operating pressure, ranging in height from 3000-900 µm as pressure changes from 1.2-6 Torr. The internal voltage drop in the plasma column is considerable, and varies with the power density and pressure. At lower pressures, the current is found to be denser at the outer edges of the electrodes, and at higher pressures the current moves to the inner edges, becoming more uniform as the power density increases. We explore the effects of these results on silicon etching performance. @FootnoteText@ @footnote 1@ C.G. Wilson, Y.B. Gianchandani, "Silicon Micromachining Using In Situ DC Microplasmas," Journal of Microelectricalmechanical Systems, Mar. 2001, pp. 50-54.

Plasma Science
Room 104 - Session PS2-MoM
Diagnostics I

Moderator: A. Kond, Nagoya University, Japan

9:40am **PS2-MoM1 Optical Emission Spectroscopy of Exhaust Stream Gases for Improved Process Control***, **G. Powell**,* Lightwind Inc.*; C.T. Gabriel,* Advanced Micro Devices

Traditional optical emission spectroscopy uses the processing plasma as the light source, limiting the application of OES to when the plasma is on. Another drawback occurs when OES is used in a plasma with a varying magnetic field, which induces signal variations that must be filtered out. We introduce here a new OES technique, where a small secondary plasma is added just downstream of the process chamber to provide a continuous OES light source. The secondary plasma generates emissions characteristic of gases flowing through the chamber or being emitted by the chamber walls, enabling continuous monitoring of species in the chamber. The monitoring can be carried out whether the main chamber plasma is on or off, giving an indication of chamber condition prior to processing a wafer. Signal oscillations from a moving magnetic field are completely removed by monitoring gases downstream of the chamber, simplifying data collection and interpretation for endpointing. Data from using the technique in a MERIE dielectric etch tool are given.

10:00am **PS2-MoM2 Peak Wafer Temperature Measurements during Dielectric Etching in a MERIE Etcher***, **C.T. Gabriel**,* Advanced Micro Devices

Using disposable instrumented SensArray APTI wafers, peak wafer temperatures were measured during plasma processing in a MERIE dielectric etch tool. An inorganic low-k dielectric etch process was studied, and many parameters were varied to determine their effect on wafer temperature. Wafer temperature rose rapidly when the plasma was turned on, approaching a stable temperature after about 30 sec. When the lower electrode temperature setpoint or the RF power setting was increased, wafer temperature increased linearly. Peak wafer decreased as backside He cooling pressure was increased. The dual-zone electrostatic chuck allows separate control of center and edge He pressure. These pressures were varied individually or together. Temperature measurements indicated that the zones give reasonably independent control of center and edge wafer temperature. The importance of monitoring and controlling wafer temperature during dielectric etching is also discussed.

10:20am **PS2-MoM3 Spatially (z)-Resolved Electron Temperatures and Species Concentrations in Inductively-Coupled Chlorine Plasmas, Measured by Trace-Rare Gases Optical Emission Spectroscopy***, **V.M. Donnelly**,* Agere Systems*; M.J. Schabel,* Bell Laboratories, Lucent Technologies

Determining the spatial dependence of charged and neutral species concentrations and energies in inductively coupled plasmas (ICP) is important for understanding basic plasma chemistry and physics, as well as for optimizing the placement of the wafer with respect to the ICP source to maximize properties such as etching rate uniformity, while minimizing charging-induced damage and feature profile anomalies. We have determined the line-integrated electron temperature (T@sub e@) and Cl-atom number density (n@sub Cl@) as a function of the distance (z) from the wafer in a chlorine ICP, using trace rare gases optical emission spectroscopy (TRG-OES). The gap between the wafer and the window adjacent to the flat coil inductive source was fixed at 15 cm. The pressure was 2, 10, or 20 mTorr (95% Cl@sub 2@, 1% ea. of He, Ne, Ar, Kr, Xe) and the inductive mode power was 340 or 900 W. The % n@sub Cl@ (100% = full dissociation of Cl@sub 2@) increased with power and was highest in the region between mid-gap and the ICP window, reaching nearly 100% at 900 W. T@sub e@ measured by TRG-OES, characteristic mostly of the high-energy (>10 eV) part of the electron energy distribution function (EEDF), peaked near the source under all conditions except 2 mTorr and 900 W, where a maximum T@sub e@ of 5.5 eV was observed at mid-gap. The fall-off in T@sub e@ away from the power dissipation region is mainly due to a preferential loss of high-energy electrons, sensed at high T@sub e@ - conditions by a relative reduction in the intensity of higher energy Ar emission. We can explain this by both local and non-local effects: Electrons lose kinetic energy in reaching the higher potential energy regions of lower electron density near the wafer (non-local effect). At higher pressures, the mean free path for inelastic scattering by high-energy electrons becomes comparable to the reactor dimensions, causing the EEDF to be relatively hot at the source and cool at the wafer (local effect).

10:40am **PS2-MoM4 Diagnostic of Silicon Etch Plasmas by Optical and Mass Spectrometry, Correlation with XPS Surface Diagnostics***, N. Sadeghi,* University Joseph Fourier-Grenoble and CNRS, France*; G. Cunge, R.L. Inglebert, L. Vallier,* LTM/CNRS (CEA-LETI), France*;* ***O. Joubert,*** CNRS, France **INVITED**

As device dimensions are continuously decreasing, the precise critical dimension control during the etch processes becomes a key issue in device fabrication. A better understanding of both plasma composition and plasma-surface interaction during the process are required to obtain a deeper insight on etch mechanisms involved in plasma etching. This work is centered on polysilicon gate etch processes using HBr/Cl@sub 2@/O@sub 2@ and HBr/Cl@sub 2@/O@sub 2@/CF@sub 4@ chemistries in an inductively coupled DPS-5200 Applied Materials reactor. The chemical composition of the layers deposited on the trench sidewalls is analyzed by quasi-insitu XPS and is correlated to the relative densities of the different neutral species present in the gas phase and to the composition of the ions impinging on the wafer surface and on the reactor walls. The following conclusions can be drawn: - Contrary to the expectations, halogen ions are not the dominant ionic species impacting on the wafer surface. Mass spectrometry measurements show that in standard etch conditions, Si@super +@ and other silicon containing ions can account by more than 50% of the total ion flux. - In HBr/Cl@sub 2@/O@sub 2@ gas mixtures, the passivation layer is formed by redeposition of silicon etch products fragmented in the plasma and then redeposited on the feature sidewalls where they get oxidized by the oxygen present in the gas phase. When CF@sub 4@ is added into the gas mixture, the passivation layer is formed by condensation of CF@sub x@ species on the feature sidewalls. - Mass spectra experiments also give some interesting information on the influence of CF@sub 4@ addition in keeping the chamber walls clean. Consequences on real processes are discussed.

11:20am **PS2-MoM6 Electrical and Plasma Property Measurements of a DRIE Bosch Process***,* ***I.C. Abraham,*** *P.A. Miller, J.R. Woodworth, C.G. Willison, R.J. Shul,* Sandia National Laboratories

We measured electrical and plasma properties of a DRIE (Deep Reactive Ion Etching) Bosch process used for micromachining bulk silicon. The DRIE process enables the patterning of high-aspect-ratio deep Si features using an iterative inductively coupled plasma (ICP) deposition/etch cycle in which a polymer etch inhibitor is conformally deposited over the wafer during the deposition cycle. The polymer deposits over the resist mask, the exposed Si field, and along the sidewall. During the ensuing etch cycle, the polymer film is preferentially sputtered from the Si trenches and the top of the resist mask due to the acceleration of ions perpendicular to the surface of the wafer. Provided that the ion scattering is relatively low, the polymer film on the sidewall is removed at a much slower rate, thus minimizing lateral etching of the Si. Both the 2 MHz ICP source and the 13.56 MHz cathode components of the floating-potential oscillations (and therefore the plasma-potential oscillations) were measured by a glass-enclosed capacitive probe immersed in the plasma. We used rf-potential and current sensors installed at the output of the chuck's matching network and a calibrated equivalent circuit model to compute the chuck potential waveform. The plasma density and electron temperature were measured using a floating double Langmuir probe. Measurements were made throughout the etch and deposition cycles of the Bosch process. Estimates of the ion energy distribution are presented. This data is expected to increase understanding of the DRIE Bosch process and ultimately improve process control. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the Department of Energy under Contract DE-AC04-94AL85000.

Semiconductors
Room 122 - Session SC+SS-MoM

Oxidation of Semiconductors

Moderator: J.E. Crowell, University of California, San Diego

10:00am **SC+SS-MoM2 Coexistence of Active and Passive Oxidation Areas on the Si(100) Surface under Oxygen Cluster Beam Impact***,* ***D.V. Daineka,*** A.F. Ioffe Physicotechnical Institute, Russia, France*; F. Pradère, M. Chatelet,* CNRS, Ecole Polytechnique, France*; E. Fort,* Universités Paris VI et Paris VII, France

The Si(100) oxidation by cluster beam impact has been studied in ultrahigh vacuum for surface temperatures from 850 to 1100°C. Neutral oxygen clusters with an average size of 2000 molecules and a translational energy of 0.26 eV/molecule were delivered by a supersonic beam with the maximal flux density of 10@super 15@ cluster/cm@super 2@s. The analysis of surface profiles after the beam exposure at T 2SiO(g), is characterized with a steep inner wall and a gradual decrease of its depth towards the outer edge. In the central part of the impact spot, surrounded by the groove, no surface etching occurs due to the formation of a protective oxide layer. The revealed effect is attributed to the gaussian flux density distribution in the cluster beam cross section. The abrupt drop of the etching rate at the inner wall of the groove corresponds to the transition from active to passive oxidation. Only active oxidation with formation of a single etch pit was observed at T>1000°C. The reaction is steady-state and close to first-order. It has been found that there is no pronounced temperature dependence of the etching rate, which is in contrast with the previous results obtained with molecular oxygen.@footnote 1,2@ Etching rates as high as 6 µm/min were measured for T>1000°C. This enhanced reaction efficiency is attributed to the role of the oxygen clusters. The obtained results show that the knowledge of the flux density distribution in the beam is extremely important when supersonic sources are used to study surface reactions. @FootnoteText@ @footnote 1@ Y. Ono, M. Tabe, H. Kageshima, Phys. Rev. B48(1993) 14291 @footnote 2@ S. Hildebrandt, A. Kraus, R. Kulla, H. Neddermeyer, Appl. Surf. Sci. 141(1999) 294 .

10:20am **SC+SS-MoM3 An Ab Initio Study of the Initial Oxidation of the Si(100)-(2x1)***, Y. Widjaja,* ***C.B. Musgrave,*** Stanford University

As the dimensions of metal-oxide-semiconductor (MOS) devices keep shrinking, O@sub 2@ molecule is increasingly used as the oxidizing species over H@sub 2@O as it oxidizes silicon more slowly and hence results in better control of film thickness. Here, we use density functional theory to investigate the detailed chemical mechanism of O@sub 2@ reaction with the Si(100)-(2x1) surface using cluster approximations, in which larger clusters are used to examine reactions across dimers as well as to investigate nonlocal effects. Our proposed mechanism confirms the trapping-mediated mechanism previously observed by molecular beam experiments. We find that O@sub 2@(g) initially adsorbs on the "up" silicon atom of the surface dimer with an adsorption energy of 31 kcal/mol. The adsorption is site specific and reaction on the "down" silicon atom is unstable. The adsorbed O@sub 2@(a) then reacts and forms a peroxide bridge structure, which subsequently dissociates and inserts into the dimer bond and the backbond. Reactions involving neighboring dimers also exhibit an adsorbed state in which the O@sub 2@(a) molecule is adsorbed in between the two silicon dimers. In addition to investigating the initial adsorption of oxygen molecules, we also study the atomistic mechanisms leading to the SiO(g) desorption observed at high temperature. The desorption barrier calculated is 65 kcal/mol, which explains the high thermal energy required before SiO(g) desorption occurs.

11:00am **SC+SS-MoM5 Oxidation of Si(100): Mechanisms of Oxygen Insertion, Migration and Agglomeration***,* ***K. Raghavachari,*** Agere Systems

Understanding the formation of thin oxides on silicon surfaces is of prime importance as developments in microelectronics demand oxide thicknesses of the order of a few atomic layers. We have carried out first-principles quantum chemical calculations with cluster models to investigate the structural and mechanistic aspects of the initial oxidation of a Si(100) surface. The microscopic steps related to the initial oxygen incorporation as well as oxygen migration and agglomeration on annealing are considered in detail. The calculated activation energy barriers suggest an interesting competition between the steps involved in oxygen insertion and oxygen migration and agglomeration. The presence of surface hydrogen causes significant perturbations on the calculated energy barriers and has important implications to the reaction mechanisms. Our results are used to provide novel interpretations of experimental infrared spectroscopic data.

11:20am **SC+SS-MoM6 Fundamental Aspects of Silicon Oxidation: O@sub 2@ and H@sub 2@O Reaction with Si(100) and H-passivated Si Surfaces***, **Y.J. Chabal,*** Agere Systems*; A. Esteve,* LAAS, France*; X. Zhang, E. Garfunkel,* Rutgers University*; K. Raghavachari,* Agere Systems

Examining the initial oxidation steps of both clean and H-passivated silicon surfaces is important to unravel the mechanism for oxygen insertion and oxide formation in realistic environments. We have combined high resolution infrared absorption spectroscopy (IRAS) with quantum chemical (QC) cluster calculations and kinetic Monte Carlo (KMC) simulations to determine the energetics and kinetics of O@sub 2@ and H@sub 2@O thermal oxidation of Si(100) and H-passivated Si(100) and Si(111) surfaces. Specific local structures are determined by comparing experimental IRAS data of both Si-O and Si-H vibrational modes with vibrational frequencies determined from first principles QC calculations of energetically stable model structures. KMC simulations are then used to analyze the cumulative effect of a series of elementary reaction steps on extended growth of an oxide layer. For the clean Si(100)-(2x1) surface, oxygen is readily incorporated into the surface from either O@sub 2@ or H@sub 2@O with a thermodynamic propensity to agglomerate but with different kinetics. KMC simulations show that oxide growth is governed by two fundamental phenomena: (i) charge transfer arising from oxygen insertion into the Si-Si bonds and (ii) hydrogen passivation and/or dangling bond formation at the surface. The charge transfer strongly affects the energetics (thermodynamics) of further oxygen agglomeration (the ability for an oxygen atom to leave an oxygenated dimer unit); the presence/absence of dangling bonds then compounds this effect by further modifying the oxygen migration kinetics. For H-passivated surfaces, both O@sub 2@ and H@sub 2@O are found to incorporate into the Si-SiH backbonds without loss of surface hydrogen. We find an oxygen insertion energy of 1.6 - 1.7 eV, while the oxidation kinetics of different surface structures appear to be dominated by O2 access to Si-Si bonds (locally blocked by unreactive Si-H species).

11:40am **SC+SS-MoM7 Displacement of Surface As Atoms by Insertion of Oxygen Atoms into As-Ga Backbonds***, **M.J. Hale,** S.I. Yi, J.Z. Sexton, A.C. Kummel,* University of California, San Diego

Stable and metastable oxide structures resulting from the reaction of GaAs(001)-(2x4) with O and O@sub 2@ are investigated using scanning tunneling microscopy (STM). The relative stability of these oxide structures is examined using density functional calculations. STM images show that when GaAs(001)-(2x4) is exposed to O atoms, the O atom will either remove an As atom from its original dimer position and take its place or insert into an As-Ga backbond and create a metastable state. As the O atom coverage increases, O atoms increasingly occupy the position of two As atoms across two neighboring dimers, while the number of metastable states remain constant. These experiments show that As is preferentially removed as a pair (As@sub 2@) with one removed As atom originating from each of two neighboring As-As dimers instead of two As atoms from the same As-As dimer. This displacement of As@sub 2@ is consistent with the propensity of the unit cell to relax into a charge-balanced morphology. Furthermore, the charge-imbalance from oxygen chemisorption is the driving force for As@sub 2@ displacement. DFT calculations demonstrate both the charge imbalances in the metastable states and the relative stability of the final chemisorption state. The displaced arsenic atoms form As@sub Ga@ antisites which pin the Fermi level and prevent thermal oxidation from forming an electrically passive interface on GaAs in contrast to vapor deposited oxides.

Semiconductors
Room 124 - Session SC-MoM
Band-Engineered Electronic Materials

Moderator: R.S. Goldman, University of Michigan

9:40am **SC-MoM1 III-N-V: A Novel Class of Compound Semiconductors for Electronic and Photonic Applications***, **C.W. Tu,*** University of California, San Diego **INVITED**

Recently there is much interest in III-N-V compound semiconductors, because only a small amount of nitrogen incorporation (less than 5%) in conventional GaAs- and InP-based III-V compounds results in very large bandgap bowing, which is mainly from the downward movement of the conduction band edge. We demonstrated that InNAsP/GaInAsP single-quantum-well microdisk lasers exhibit a large characteristic temperature, as a result of a large conduction band discontinuity and electron confinement in the quantum well. An application of more interest is using GaInNAs/GaAs heterostructures on GaAs substrates for 1.3 micron edge-emitting and vertical-cavity surface-emitting lasers (VCSELs), utilizing the well developed GaAs/AlAs distributed Bragg reflectors (DBRs). We demonstrated even longer wavelength (1.5 micron) room-temperature photoluminescence (PL) from self-assembled GaInNAs QDs. We have also utilized the low-bandgap GaInNAs as the base of a heterojunction bipolar transistor (HBT), which exhibits a 0.4 V reduction in the turn-on voltage for low-power applications. Besides bandgap bowing, incorporating nitrogen in GaP also results in a change in the band structure. We have demonstrated that with only 0.5% nitrogen, the Ga(N)P bandgap changes from being indirect to direct, with strong PL emission in the red (650 nm). We have fabricated light-emitting diodes (LEDs) from GaNP/GaP heterostructures grown with one-step epitaxy, which is simpler than the commercial process of GaAs substrate removal and wafer bonding to a transparent GaP substrate for high-brightness AlInGaP LEDs. We are also exploring GaInNP on GaAs for HBT applications because of near-zero conduction band offset.

10:20am **SC-MoM3 Microstructure and Optical Properties of (InGa)(AsN) Alloys and Nanostructures***, **X. Weng,** S. Clarke, A. Daniel, J. Holt, S. Krishna, S. Kumar,* University of Michigan, Ann Arbor*; J. Sipowska,* University of Michigan, Flint*; V. Rotberg, R. Clarke, A. Francis, P.K. Bhattacharya, R.S. Goldman,* University of Michigan, Ann Arbor

Mixed anion nitride-arsenide compound semiconductor heterostructures are promising for devices with emission or detection wavelengths throughout the near infrared range. However, a limited miscibility of InGaAsN on the anion sublattice leads to the formation of phase separation-induced alloy nanostructures.@footnote 1,2@. We have synthesized InGaAsN alloys and nanostructures by N ion implantation into GaAs and InAs, with a variety of implantation and rapid thermal annealing conditions. We have analyzed the composition, structure, and properties of the resulting alloys and nanostructures, using nuclear reaction analysis, transmission electron microscopy (TEM), x-ray energy dispersive spectrometry, x-ray diffraction, photoluminescence, and cathodoluminescence spectroscopy. For 50 keV N ion implanted GaAs and InAs substrates, high resolution cross-sectional TEM reveals ~5nm diameter amorphous nanostructures surrounded by crystalline matrices. For 100 keV N ion implanted GaAs epilayers, crystalline nanostructures surrounded by disordered matrices are apparent. Electron and x-ray diffraction indicate that these nanostructures are cubic phases with lattice parameters similar to that of pure GaN. The crystalline nanostructures exhibit significant photoluminescence in the near infrared range. The apparent lowering of the fundamental band gap of the GaN nanostructures is consistent with strain-induced band gap narrowing of a GaN-rich cluster.@footnote 1@. We will discuss the mechanisms of formation and coarsening of these nanos truc tures, correlations between their optical and structural properties, and comparisons with similar alloys and nanostructures synthesized by molecular beam epitaxy. @FootnoteText@@footnote 1@R. S. Goldman et al., Appl. Phys. Lett. 69, 3698 (1996), J. Electr. Mater. 26, 1342 (1997). @footnote 2@H. P. Xin et al., Appl. Phys. Lett. 74, 2337 (1999).

10:40am **SC-MoM4 Measurement of Charge Separation Potentials In GaAs(1-x)N(x)***, **S.W. Johnston,** R.K. Ahrenkiel,* National Renewable Energy Laboratory*; C.W. Tu, Y.G. Hong,* University of California, San Diego

The ternary alloy GaAs(1-x)N(x) is interesting as a semiconductor that can be grown epitaxially on GaAs. As is well known, the bandgap can be reduced by as much as 0.4 eV by changing the nitrogen concentration from 0% to 3%. We measured the spectral response and photoconductive lifetime of the alloys, as a function of temperature. In this work, the films were grown by gas-source molecular beam epitaxy on semi-insulating GaAs substrates. All measurements were made using the contactless, resonant-coupled photoconductive decay (RCPCD) method. Our data shows that the spectral or excitation spectra of GaAs1-xNx alloys consists of photoconductive band tails that extend well into the infrared (beyond the nominal bandgap). For example, the photoconductive bandtails extend to about 1.8 mm for GaAs(0.97)N(0.03). The primary photoconductive decay times are in the range of 200 to 300 ns. At temperatures below about 200 K, the decay rate begins to decrease with lowered temperature. By plotting the inverse lifetime versus 1/T, one generates the standard Arrhenius plot of a thermally activated process. These data fits produce activation energies that increase with the N-content. The activation energies, DE, for compositions x = 0.011, 0.023, and 0.033 are 67, 72, and 83 meV, respectively. These energies represent the potential barriers which inhibit recombination. The increase of DE with x is indicative of charge separation being related to N-atom clustering. Our model suggests that these barriers originate from the inhomogenous band structure produced by the random distribution of the nitrogen impurity.

11:00am **SC-MoM5 Characterization of GaPN Layers Grown by Molecular Beam Epitaxy on Si Substrates*, M.A. Santana-Aranda,*** *M. Melendez-Lira, M. Lopez-Lopez,* Centro de Investigacion y de Estudios Avanzados del IPN, Mexico*; K. Momose, H. Yonezu,* Toyohashi University of Technology, Japan*; S. Jiménez-Sandoval,* Cinvestav-IPN, Unidad Querétaro, Mexico

The heteroepitaxial growth of III-V-N alloys with high crystal quality on Si substrates could make possible the monolithic integration of III-V-N based light-emitting devices with the Si based microelectronics. However the III-V-N/Si heteroepitaxy present serious problems like the lattice mismatch and the difference in thermal expansion coefficients. In order to solve these problems, we have been studying the growth of GaPN with a N concentration of 2% that is lattice-matched to the Si substrate. The epilayers were grown by molecular beam epitaxy employing an RF plasma source to produce active nitrogen species. First, a 3.2µm Si homoepitaxial layer was grown on the substrate, followed by a thin (20nm) GaP layer to avoid the strong interaction of nitrogen with Si. Then, the GaP@sub 0.98@N@sub 0.02@layer was grown with a thickness of 400nm. In order to avoid the generation of crystal defects induced by the different thermal expansion coefficients the epilayer was capped first with a 16nm thick GaP layer and finally with a 300nm thick Si layer. The structural and optical properties of this sample were compared with those of a GaPN layer on GaP/Si but without the capping layers, and with those of a GaPN layer on a GaP substrate. Transmission electron microscopy showed that the capped heterostructure was free of crystal defects. While the other samples presented dislocations and cracks. The photoluminescence at 10K associated to GaP was blue shifted in the capped structure confirming that the GaP layers were coherently strained to the Si lattice. Raman spectroscopy showed narrow peaks in the capped structure reflecting the high structural quality of this sample, for the other samples the Raman peaks were wide suggesting the presence of disorder.

11:20am **SC-MoM6 Nanoscale Phase Formation at Cu(In,Ga)Se@sub 2@ Surfaces*, Y.M. Strzhemechny,*** *G.H. Jessen, J.I. Choi, L.J. Brillson,* The Ohio State University*; D.-X. Liao, A. Rockett,* University of Illinois at Urbana-Champaign

Copper indium gallium diselenide (CIGS) exhibits unique optical properties that make it well suited for thin film devices as a polycrystalline material. The engineered electronic properties of CIGS heterojunctions depend sensitively on the CIGS near-surface region. The nanoscale electronic structure and chemistry of this layer and, specifically, point defect segregation and surface phases are thought to be critical to such device structures, yet they are relatively unexplored. We employed low-energy depth-resolved cathodoluminescence (CL) and Auger Electron Spectroscopy (AES) to measure the local band and defect properties as well as composition variations of CIGS films grown epitaxially with (001), (110), and (112) orientations on GaAs wafer substrates. CL spectra reveal near band edge (NBE) emissions of 1.10 to 1.15 eV, depending on growth and orientation as well as the presence of a deep-level transition with energy 0.89-0.93 eV confined to within a few hundred nm of the free CIGS surface. The NBE energies vs. AES compositions agree with the reported variation in band gap vs. Cu/(In+Ga) ratio. The deep defect-associated feature relative to the higher lying peak has maximum intensity at the surface and decreases exponentially into the bulk with a decay length of ca. 50 nm. Auger depth profiles for (110) and (001) orientations show 16% and 20%, respectively, depletion in Cu content within tens of nanometers of the surface. Deep level and NBE energies exhibit a strong dependence on surface Cu and Ga content. Both increase by tens of meV away from the free surface, in line with the increased band gap and changes in composition. The Cu-deficient surface layers are consistent with an ordered vacancy compound proposed for the CIGS surface. The observed gap and composition changes confirm the existence of a nanoscale surface phase whose properties can impact charge generation and recombination for solar energy-generating structures.

11:40am **SC-MoM7 Metal-organic Vapor Phase Epitaxial Growth and Photoluminescent Properties of ZnMgO and ZnCdO Thin Films*, W.I. Park,*** *G.-C. Yi,* Pohang Univ. of Science and Technology, Korea (ROK)

ZnO, a wide-gap semiconductor oxide, has attracted considerable attention due to its large exciton binding energy (~60 meV) and bond strength, which might make reliable high efficiency photonic devices based on ZnO. Recently it has also been reported that ZnMgO was grown with maximum Mg incorporation up to 36 at.% without phase separation and that the room temperature luminescence energy in this film blue-shifted from 3.3 to 4.0 eV. Since a ZnMgO containing MgO over 4 at.% is in a thermodynamically metastable state, this result indicates that the solubility limit of Mg in ZnO depends on growth mechanisms as well as growth conditions. Meanwhile, current research on the growth of ZnO-related alloys is restricted to pulsed laser deposition and molecular beam epitaxy. Despite the epitaxial growth of high quality ZnO and related alloys using the methods, they might have disadvantages in mass production, due to high cost and low throughput. In this talk, we demonstrate that metal-organic vapor phase epitaxy (MOVPE), which has great advantages in terms of large area deposition and atomic composition control feasibility, is an excellent technique for the epitaxial growth of high quality ZnO and related alloy films. In addition, the structural and optical characterizations of ZnMgO and ZnCdO thin films will be reported. By increasing Mg content up to 47 at.%, the c-axis constant of ZnMgO films decreased from 0.521 nm to 0.515 nm and no significant phase separation in the ZnMgO films was observed as determined by x-ray diffraction measurements. Furthermore, the near-band-edge (NBE) emission peak position showed blue shifts of 100, 430, and 570 meV at Mg content levels of 9, 21, and 47 at.%, respectively. Photoluminescent properties of the ZnMgO and ZnCdO alloy films will also be discussed.

Surface Engineering
Room 132 - Session SE-MoM
Nanocomposites, Multilayers, & Nanostructured Materials

Moderator: G.J. Exarhos, Pacific Northwest National Laboratory

9:40am **SE-MoM1 Magnetron Sputtered W/C Films with C@sub 60@ as Carbon Source*, J.-P. Palmquist,*** Uppsala University, Sweden*; M. Oden, Zs. Czigany, J. Neidhart, L. Hultman,* Linköping University, Sweden*; U. Jansson,* Uppsala University, Sweden

Thin films in the W-C system have been prepared by magnetron sputtering of W with co-evaporated C@sub 60@ as carbon source. We have previously demonstrated epitaxial growth of several binary and ternary metal carbides as well as superlattice structures and gradient films at very low deposition temperatures (100-500 oC). In this study, we present the first results of epitaxial deposition of several phases in the W-C system. In addition, nanocrystalline tungsten carbide films can be deposited. At low C@sub 60@/W ratios, epitaxial growth of @alpha@-W with a solid solution of carbon was obtained on MgO(001) and Al@sub 2@O@sub 3@(0001) at 400 oC. The carbon content in these films (10-20 at%) was at least an order of magnitude higher than maximum equilibrium solubility and gives rise to an extreme hardening effect. Nanoindentation measurements showed that the hardness of these films increased with the carbon content and values as high as 35 GPa were observed. At high C@sub 60@ /W ratios, films of the cubic @beta@-WC@sub 1-x@ (x = 0-0.6) phase was deposited. This phase is not thermodynamically stable at T< 2500 oC but is frequently observed in thin film deposition. The microstructure of the @beta@-WC@sub 1-x@ films was dependent on the deposition conditions. At high deposition rates, nanocrystalline films with a grain size <30 Å were obtained in the temperature range 100-800 oC. The hardness of these films varied from 14 to 24 GPa. Also, for the first time, we have demonstrated epitaxial growth of single-crystalline @beta@-WC@sub 1-x@ films on MgO(001) at very low deposition rates, ~5 Å/min. Finally, at intermediate C@sub 60@/W ratios, epitaxial films of hexagonal W@sub 2@C was deposited on MgO(111), while polycrystalline phase mixtures was obtained on other substrates.

10:20am **SE-MoM3 Synthesis and Characterization of Thermally Stable TiB@sub 2@/TiC Nanolayered Superlattice Coatings for Dry Machining Applications*, K.W. Lee,*** Northwestern University, US*; Y.H. Chen, Y.-W. Chung, K. Ehmann, L.M. Keer,* Northwestern University

It was demonstrated from previous studies that nanolayered superlattice coatings with the correct choice of components and layer thicknesses have enhanced hardness, due to interfaces providing barriers against dislocation motion and multiplication. We expect superlattice coatings made of two immiscible components to be stable against interdiffusion. Therefore, the layer structure and reasonable hardness for such superlattice coatings should be preserved at high temperatures. These thermally stable coatings are desirable for protection of cutting tools in dry machining applications, which may operate at temperatures in the 800 â€“ 1000 C regime or higher. For this reason, TiB@sub 2@ and TiC were chosen for this investigation. Nanolayered coatings made of these two immiscible components were synthesized by dc dual-cathode magnetron sputtering. Substrate rotation was used to enhance uniformity of the coating.

Substrates included silicon, M2 steel and WC cutting inserts. Superlattice coatings with TiB@sub 2@ (001) and TiC (111) preferred orientations on Si (001) were synthesized. Transmission electron microscopy studies showed that the layer structure of the coating was preserved after annealing in vacuum at 1000 C for one hour. Room-temperature hardness of these coatings approaches 50 GPa, far exceeding the rule-of-mixture value. Coatings synthesized using the substrate rotation system have improved surface smoothness and reduced internal stress. Wear and durability tests on coated M2 steel and WC cutting inserts demonstrated the improved tribological performance of these coatings under unlubricated conditions compared with other standard coatings such as TiN.

10:40am **SE-MoM4 Chemical Vapor Deposition and Characterization of TiO@sub 2@ Nanoparticles***, **W. Li**, S.I. Shah, C.P. Huang,* University of Delaware*; O.J. Jung,* Chosun University, South Korea

Chemical vapor deposition (CVD) was used to deposit TiO@sub 2@ nanoparticles with and without metal ion dopants. X-ray photoelectron spectroscopy (XPS) and X-ray energy dispersive spectroscopy (EDS) experiments confirmed the TiO@sub 2@ chemical composition. X-ray diffraction (XRD) patterns showed the polycrystalline anatase structure of TiO@sub 2@. Transmission electron microscopy (TEM) revealed that these particles are nanosized with an average diameter of approximately 20-30 nm. The nanosized particles can provide a large surface to volume ratio and large number of free surface charge carries which are crucial for the enhancement of photocatalytic activity. In order to improve the photocatalysis efficiency, Pd@super 2+@, Pt@super 2+@, Nd@super 3+@ and Fe@super 3+@ transition metal ion were also incorporated as dopants. The effects of dopants on photocatalytic kinetics were investigated by studying the degradation of 2-chlorophenol (2CP) with an ultraviolet light source. The results showed that doped TiO@sub 2@ nanoparticles have higher photocatalytic efficiency than those without dopants with Nd3+ showing the highest efficiency. Time of 90% destruction of 2CP was reduced by one half with Nd3+ doping when compared with undoped TiO@sub 2@.

11:00am **SE-MoM5 Nanocomposite Tribological Coatings with "Chameleon" Surface Adaptation***, **A.A. Voevodin**, J.S. Zabinski,* Air Force Research Laboratory **INVITED**

Composite coatings where hard nanocrystalline grains are embedded in an amorphous matrix provide considerable improvement in hardness, toughness, wear resistance, and friction reduction. A review of their design concepts is provided with a focus on: (1) improvement in toughness characteristics; and (2) adaptive tribological behavior. Embedding small 5-20 nm hard nanocrystalline grains in an amorphous matrix helps to arrest crack development and introduces ductility through grain boundary sliding. Matrix materials may be selected to provide adaptation of the surface chemistry and/or microstructure to variations in environment and loading conditions to mantain tribological properties. Such materials have been coined chameleon coatings. A combination of nanocrystalline TiC and WC embedded into an amorphous diamond-like carbon (DLC) matrix enabled the coatings to adjust their mechanical response from hard to ductile and significantly reduced the danger of brittle failure. A similar concept was used to improve toughness of composite coatings made of nanocrystalline yttria-stabilized zirconia (YSZ) embedded in an amorphous YSZ/Au matrix. In another example, a combination of nanocrystalline WC and WS2 in an amorphous DLC matrix exhibited surface chemical and microstructural self-adjustment in sliding contact when test environment was cycled from humid to dry. This coating could repeatedly adjust its surface from hexagonal WS2 for sliding in dry nitrogen or vacuum environments to graphitic carbon for sliding in humid air, maintaining a low friction coefficient in both environments. The YSZ/Au nanocomposite developed a gold rich surface layer during heating at 500 °C in air, which considerably improved YSZ tribology in temperature cycling. This coating was further doped with MoS2 and carbon to obtain an environmental adaptation similar to that in the WC/DLC/WS2 system. Chameleon coating designs and applications for advanced tribological coatings are discussed.

11:40am **SE-MoM7 Nanometer-size Monolayer and Multilayer Molecule Corrals on HOPG: A TOF-SIMS, XPS and STM Study***, **Y.J. Zhu**, T.A. Hansen, S. Ammermann, J.D. McBride, T.P. Beebe, Jr.,* University of Utah

The surface chemistry of highly oriented pyrolytic graphite (HOPG) bombarded with energetic Cs@super +@ ions was studied using the combined surface analysis techniques of TOF-SIMS, (time-of-flight secondary ion mass spectrometry), XPS (x-ray photoelectron spectroscopy) and STM (scanning tunneling microscopy). Controlled surface modification and defect production were achieved by bombardment of HOPG with Cs@super +@ ions at various energies and at various dose densities. XPS shows cesium implanted into HOPG exists in an oxidized state. The Cs@super +@ bombardment of HOPG enhances oxygen adsorption due to both the dissociative adsorption of oxygen at defect sites produced by Cs@super +@ ions, and by the formation of cesium oxide. The surface coverage of cesium on HOPG increases linearly with increasing Cs@super +@ dose density at low bombardment energies, and decreases rapidly with increasing Cs@super +@ bombardment energy due to cesium implantation below the surface. The thermal stability of cesium in HOPG has a complex behavior at elevated temperatures. Defects created by Cs@super +@ ion bombardment in HOPG were subsequently oxidized at 650 @super o@C in air to controllably produce nanometer-size monolayer and multilayer molecule corrals (etch pits). Multilayer pits can be produced using higher energy Cs@super +@ ion bombardment, and monolayer pits can be produced using lower energy Cs@super +@ ion bombardment. The pit density, pit yield, pit diameter and pit depth can be controlled by varying experimental conditions, and they were studied systematically by STM. The measured depth-resolved growth rates for multilayer pits are in good agreement with the model of the growth rate acceleration by adjacent layers. The results obtained lead to a better understanding of the kinetics and mechanism of the graphite oxidation reaction, and more importantly to the accurate production and control of nanometer-size monolayer and multilayer molecule corrals on HOPG.

Surface Science
Room 120 - Session SS1-MoM
Aerosol and Related Chemistry

Moderator: T.E. Madey, Rutgers, The State University of New Jersey

9:40am **SS1-MoM1 Great Enhancements in Dissociative Electron Attachment to Chlorofluorocarbons Adsorbed on Polar Molecular Ices: A New Pathway for the Formation of the Ozone Hole***, **Q.-B. Lu**,* University of Sherbrooke, Canada*; T.E. Madey,* Rutgers University*; L. Sanche,* University of Sherbrooke, Canada **INVITED**

Atmospheric ozone depletion is an issue of global concern. It is generally accepted that the Earth's ozone layer is depleted by chlorine atoms produced via photolysis of chlorofluorocarbons (CFCs) in the upper stratosphere, and the formation of the Antarctic / Arctic ozone hole has been attributed to heterogeneous reactions occurring on surfaces of ice particles in polar stratosphere clouds (PSCs). Based on measurements of anion yields in (~250 eV) electron stimulated desorption (ESD) from a submonolayer of CFCs coadsorbed with polar molecules, we find evidence for an unrecognized process: dissociative electron attachment (DEA) to CFCs by low energy secondary electrons is enhanced by several orders of magnitude when CFCs are adsorbed on polar molecular ices, such as water and ammonia.@footnote1,@@footnote2@ This enhancement has been identified to be due to transfer of ~ 0 eV electrons temporarily trapped in polar molecular ices to CFCs that then dissociate via DEA, based on measurements of electron trapping cross sections as a function of electron energy in the range of 0-10 eV.@footnote3@ This enhancement effect should be very efficient in the stratosphere, where low-energy electrons can be produced by cosmic-ray ionization and trapped in PSCs. In this talk, we present our laboratory measurements on anion yield enhancements in ESD and on absolute DEA cross sections of CFCs adsorbed on polar molecular ices, and discuss the physics of these processes. The implications of these observations for the formation of Antarctic / Arctic ozone holes, and correlations with data obtained by field measurements (satellite, balloon and ground station), will also be discussed. @FootnoteText@ @footnote1@ Q.-B. Lu and T.E. Madey, Phys. Rev. Lett. 82, 4122(1999); J. Chem . Phys. 111, 2861(1999). @footnote2@ Q.-B. Lu and T. E. Madey, Surf. Sci. 451, 238(2000); J. Phys. Chem. B105, 2779(2001). @footnote3@ Q.-B. Lu and L. Sanche, Phys. Rev. B63, 153403(2001).

10:20am **SS1-MoM3 Electron Stimulated Reactions of Chlorocarbons in Ice Films***, **H. Fairbrother**, A.J. Wagner,* Johns Hopkins University

Electron stimulated reactions of chlorocarbons adsorbed in ice films are of importance in atmospheric processes as well as in understanding the mechanisms of glow discharge chlorocarbon remediation. We present results on the electron -induced reactivity of carbon tetrachloride (CCl@sub 4@) adsorbed in ice films at 100K studied using a combination of reflection absorption infrared spectroscopy and mass spectrometry. Both mass spectrometry and infrared measurements indicate that CCl@sub 4@ is converted to a mixture of phosgene (COCl@sub 2@), CO@SUB 2@ and HCl as a result of electron mediated reactions within the ice/chlorocarbon film, supported by separate experiments using @super 13@CCl@sub 4@. The product branching between COCl@sub 2@ and CO@SUB 2@ was found to be sensitive to the initial H@sub 2@O:CCl@sub 4@ mixture, with H@sub2@O-rich films favoring CO@SUB 2@ production. Results will also be presented on the electron-stimulated reactions of CHCl@sub 3@, CH@sub 2@Cl@sub 2@ and CH@sub 3@Cl adsorbed in ice films.

10:40am **SS1-MoM4 Study of CO@sub 2@ Adsorption on Ice using High-pressure X-ray Photoelectron-spectroscopy**, ***F. Requejo***, Lawrence Berkeley National Laboratory; *H. Bluhm*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany; *D.F. Ogletree, M. Luna, Z. Hussain*, Lawrence Berkeley National Laboratory; *C.S. Fadley*, University of California, Davis; *M. Salmeron*, Lawrence Berkeley National Laboratory

Water at surfaces plays a fundamental role in atmospheric science, chemistry and biology. A new generation of experimental and theoretical tools are actually revisited this subject.@footnote 1@ Many interesting properties of water still remain unexplained at molecular level, even though it has been a capital subject of research for decades. Interaction between ice surfaces and adsorbed molecules emerges as a very attractive topic. Macroscopic studies@footnote 2@ have investigated the adsorption of CO@sub 2@ on ice, showing the existence of a quasi-liquid layer on ice. On the other hand, new studies@footnote 3@ confirm that CO@sub 2@ is the main driver in global warming and glaciation changes. Recently, by means of surface X-ray absorption spectroscopy, we have studied the premelting of ice trough to the Auger electron yield NEXAFS from its surface. This methodology has proven to be capable of detecting and measuring the thickness of the liquid layer on ice. In the present contribution, we have applied the same methodology to study the effect of atmosphere CO@sub 2@ on the premelting of ice. Samples of ice and water were condensed from vapor onto a cooled substrate, which was placed inside a cell. In equilibrium conditions between the water vapor and the sample at different temperatures, CO@sub 2@ gas was introduced into the cell at different pressures in the range of 0 to 1 Torr. Afterwards, surface-sensitive XPS measurements and Auger electron-yield NEXAFS experiments at O K-edge in the energy range of 530 to 620 eV were performed. Our results indicate unambiguously that the amount of liquid water on the surface of ice increases with the pressure of CO@sub 2@. This effect becomes more evident when the temperature is also increased. @FootnoteText@ @footnote 1@ F. Bensebaa and T.H. Ellis. Progr. in Surf. Sc., 50, 1-4 (1995) 173. @footnote 2@ J. Ocampo and J. Klinger. J. Coll. Interf. Sci. 86, 2 (1982) 377. @footnote 3@ N.J. Shackleton. Science, 298 (2000) 1897. F.G. Requejo - Postdoctotoral Fellow at MSD, LBNL. Berkeley, CA. Permanent address: Dept. Physics, FCE, UNLP and IFILP(CONICET), La Plata, Argentina.

11:00am **SS1-MoM5 Sea Salt Aerosol Reactions: Quantitative Single Particle Studies**, *A.J. Laskin, M.J. Iedema*, ***J.P. Cowin***, Pacific Northwest National Laboratory

Sea salt from ocean wave action is a very common aerosol. This aerosol is far from inert, with several papers in recent years looking at how it can react with HNO3 to form sodium nitrate (releasing HCl), or hydroxyl radicals to form Cl2. We present highly quantitative, time resolved studies of sea salt aerosols observed during the fall 2000 Texas Air Quality Study. We used a novel automated sampler to preserve 3000 samples (10 minute intervals) for nearly a month of continuous observation. These were preserved for automated laboratory analysis with scanning electron microscopy/energy dispersed x-ray analysis. We analyze particles down to 0.2 micron in size for elements from carbon upward. We are able to follow these reactions in detail, and relate them to the time-resolved atmospheric gases seen by other researchers there. We are able to show that nitration occurs preferentially to sulfating (until later in the daily cycle). We are able to follow the size-resolved reaction, with as expected faster reactions for the smaller particles. We used the archived samples for other techniques too. High resolution time of flight secondary ion mass spectrometry gave important molecular speciation information, on a single particle basis (0.2 micron resolution).

11:20am **SS1-MoM6 Surface Chemistry of Size-Selected, Gas-Phase Nanoparticles**, ***J.T. Roberts***, *K. Higgins, M.R. Zachariah, H. Jung*, University of Minnesota

A method has been developed to conduct surface chemistry and extract surface kinetic rates from size-selected aerosol nanoparticles. The measurements encompass broad ranges of particle size, phase, and composition. Results will be presented on the growth and oxidation of soot nanoparticles (particle radius between 10 and 40 nm). The particles are investigated for changes in surface area using on-line nanoparticle characterization instrumentation. Experiments emphasize two classes of reactive conditions: high temperature oxidation by O@sub 2@ and NO@sub x@, and room temperature addition of hydrocarbons. We believe these to be the first measurements of soot oxidation and condensation kinetics that have been conducted on size-selected particles. The results are important because soot emission from combustion sources is dictated by the competing surface processes of growth and oxidation. More generally, the results represent one of the first kinetic and mechanistic studies of gas-phase particle reactivity.

11:40am **SS1-MoM7 Scanning Electron Microscopy Studies of the Hydration of Mixed Alkali Halide Aerosols**, ***S.A. Joyce***, Los Alamos National Laboratory; *J.P. Cowin, J.T. Atherley*, Pacific Northwest National Laboratory

The morphologies of aerosols generated from pure NaCl, NaBr, and MgCl@sub 2@ solutions and from NaCl/NaBr and NaCl/MgCl@sub 2@ mixtures have been studied using an environmental scanning electron microscope (ESEM). For aerosols produced by nebulizing pure NaCl solutions, nearly perfect cubic crystals with widths of a few microns are normally observed. Upon raising the water vapor pressure in the specimen chamber, these pure NaCl aerosols are observed to dissolve at relative humidities consistent with previous studies. For aerosols produced by nebulizing NaCl/NaBr mixtures, ranging from 0.1 to 0.5 mole fraction NaBr, polycrystalline particles are often observed. For these polycrystalline samples, deliquescence of individual crystallites occurs at two different relative humidities. The central or core crystallite typically dissolves at relative humidities similar to that for pure NaCl, whereas the outer crystallites dissolve at humidities lower than that for either pure NaCl or NaBr. The deliquescence pressure for these crystallites is independent of the mole fraction of starting solution. The outer region, which dehydrates last, is composed of the NaCl/NaBr eutonic (0.9 mole fraction NaBr), with the inner region composed of nearly pure NaCl. For the aerosols produced by nebulizing NaCl/MgCl@sub 2@ mixtures, a crystalline core surrounded by a featureless outer region is typically observed. X-ray fluorescence measurements show that this outer region is largely magnesium-based while the inner crystallite in sodium-based. Based on available thermodynamic data, no eutonic of NaCl/MgCl@sub 2@ exists, and so phase separation into the pure components is expected. The implication of the phase-separation to surface enrichment of minority components and its potential role in heterogeneous atmospheric chemistry will be discussed. * Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

Surface Science

Room 121 - Session SS2-MoM

Metal Clusters

Moderator: C.F.O. Bostedt, Lawrence Livermore National Laboratory

9:40am **SS2-MoM1 Mesoscopic Strain-Induced Magic Fe Nanostructures on Cu(100)**, *N. Lin, A. Dmitriev*, Max-Planck-Institut for Solid State Physics, Stuttgart, Germany; *V.S. Stepanyuk, D.I. Bazhanov*, Martin-Luther-University, Germany; *J. Weckesser*, Max-Planck-Institut for Solid State Physics, Stuttgart, Germany; ***J.V. Barth***, EPFL, Switzerland; *K. Kern*, Max-Planck-Institut for Solid State Physics, Stuttgart, Germany and EPFL, Switzerland

We report a novel phenomenon in metal-on-metal heteroepitaxy, expressed in the arrangement of Fe islands grown at low temperature (<200K) on a Cu(100) surface. Scanning tunneling microscopy observations reveal that Fe atoms aggregate as perfectly oriented well-defined nanometer-scale arrays when Fe-Cu exchanging is inhibited. The basic unit of these nanoarrays is a tetramer of Fe atoms. More than 60 percent of the nanoarrays consist of four tetramers arranged in a square shape, aligning exactly to the high symmety directions of the Cu(100). The sharp distribution and distinct shapes of the nanoarrys can be understood in the framework of mesoscopic strain. STM and first principle calculations demonstrate that both the Fe isalnds and Cu substrate experience a large relaxation due to the mesoscopic strain: the Fe interatomic distance in the tetramers (2.0 Å) is 20% less than that in thin fcc Fe/Cu(100) films (2.5 Å), and the Cu substrate underneath the Fe nanoarrays is compressed 16.4% relative to the unrelaxed Cu surface (2.56 Å) . The giant compression and the high stress energy promote the formation of super-compressed Fe tetramers and their aggregation as magic nanoarrays with regular shape and orientation.

10:00am **SS2-MoM2 Nanostructed Growth of Metal Clusters on Ultrathin Al@sub 2@O@sub 3@ Films on Ni@sub 3@Al(111)***, **A. Rosenhahn,*** Lawrence Berkeley National Laboratory*; A. Wiltner,* Universitaet Bonn, Germany*; K. von Bergmann,* Universitaet Hamburg, Germany*; J. Schneider,* Lawrence Berkeley National Laboratory*; C. Becker,* Universitaet Bonn, Germany*; B.S. Mun,* Lawrence Berkeley National Laboratory*; F.J.G. de Abajo,* Centro Mixto CSIC-UPV/EHU*; M.A. van Hove, C.S. Fadley,* Lawrence Berkeley National Laboratory*; K. Wandelt,* Universitaet Bonn, Germany

Highly ordered, ultrathin alumina films can be grown on Ni@sub 3@Al(111) by simply exposing the alloy surface to oxygen at high temperatures.@footnote 1@ Because of the conductibility of the thin films, the properties of metal aggregates on the surface of these oxide films can easily be studied without charging of the surface. Using STM, we have investigated the nucleation properties of different types of metals reaching from very noble ones like Ag, Au, and Cu to metals which are more reactive towards oxygen like V and Mn. All clusters show preferred nucleation on distinct sites of the oxide film.@footnote 2@ As long as the oxide is not entirely covered by metal, two different mean cluster distances of 2.5 nm and 4.6 nm can be found. The distribution of the clusters on the surface reveals a hexagonal symmetry. The same periodicity can be found on the metal-free oxide film, depending on the applied bias voltage.@footnote 3@ As these superstructures reveal the same symmetry and periodicity as the cluster distribution, the nucleation is clearly determined by these sites. Because the superstructures are just at certain bias voltages visible, the prefered nucleation is not simply due to a modulation of the morphology. We will discuss, in which way the structure of the oxide film and the nucleation of the metal clusters are correlated. @FootnoteText@ @footnote 1@ A. Rosenhahn, J. Schneider, C. Becker, and K. Wandelt, J. Vac. Sci. Technol. A 18(4), 1923 (2000). @footnote 2@ C. Becker, K. v. Bergmann, A. Rosenhahn, J. Schneider, K. Wandelt, Surf. Sci. Lett., in Press. @footnote 3@ A. Rosenhahn, J. Schneider, J. Kandler, C. Becker, and K. Wandelt, Surf. Sci. 433-435, 705 (1999).

10:20am **SS2-MoM3 Nanocatalysis:Tuning Efficiency and Selectivity Atom-by-Atom***, **U. Heiz,*** University of Ulm, Germany **INVITED**

The preparation of a collection of supported metallic particles that are truly monodisperse, i.e. they all have exactly the same size, has long considered to be virtually impossible. As a consequence it has been difficult to recognize size effects for small supported clusters, as size distributions have been broad. For clusters in the gas phase, however, strong size-dependent chemical properties have been discovered during the last two decades and the obtained results lead to new concepts for understanding their chemical properties. Connections of these observations with real catalysis has often been stressed and suggestions for tuning efficiency and selectivity of a certain catalytic process by simply changing cluster size were made already in early days. Efficient and selective conversion is indeed important in catalysis, as most catalytic surfaces assist a variety of reactions. It is therefore of interest to study the factors affecting the size-dependent selective and efficient behavior of catalytic systems. We succeeded to prepare model catalysts consisting of a collection of metal particles of a single size. In these experiments metal atoms and small metal clusters are formed in the gas phase, size-selected and then deposited on thin MgO and TiO2 films grown on metal surfaces. Various chemical reactions on the obtained cluster-assembled materials are then investigated under UHV conditions by means of thermal desorption and infrared spectroscopies. Oxidation and polymerisation reactions are strongly dependent on cluster size and on the cluster-support interaction, and not only the number of product molecules per cluster is changed, but also the branching ratio of certain reactions. In many cases the measured reactivities are different from the ones obtained for the corresponding bulk systems. By combining the obtained experimental results with ab-initio calculations, a picture of the size-dependent behavior of cluster-assembled materials is now emerging.

11:00am **SS2-MoM5 Ion Beam Deposition of Size-selected Supported Metal Clusters***, **M. Aizawa**, S. Lee, S.L. Anderson,* University of Utah

We describe an experimental setup that allows us to investigate physical and chemical properties of supported metal clusters on various substrates at low impact energies(<10eV/atom). The metal cluster ions are generated by a laser ablation source, mass selected, and deposited on substrates. The performance of this instrument is illustrated with supported metal clusters (V, Ni, and Ir) on titania and graphite. Electronic structure of the supported metal clusters and chemical reactions over them will be studied by XPS and TPD, respectively, in terms of cluster size, impact energy and substrate defects.

11:20am **SS2-MoM6 Decay Characteristics of Surface Nanostructures: (100) vs (111) Surfaces@footnote 1@***, **J.F. Wendelken,*** Oak Ridge National Laboratory*; M. Li, B.-G. Liu, E.G. Wang,* Chinese Academy of Sciences*; Z. Zhang,* Oak Ridge National Laboratory

The stability of nanostructures after their creation is a critical issue for nanotechnology. Here we study the fundamental mechanisms of atomic scale mass transport on surfaces with regard to the instability of surface nanostructures. Pyramidal mounds were created on Cu(100) and (111) surfaces at 297 K by molecular beam deposition of Cu atoms. The stability of the nanoscale mounds was then observed with a scanning tunneling microscope for up to 24 hours. Movies produced from sequential scans show that the mounds are unstable and the decay process is profoundly different for the (100) and (111) surfaces. Decay of the (100) mounds proceeds with removal of atoms from the base of the mounds and subsequent transport to the bottom of pyramidal holes with the result that the mound walls become steeper with time. In contrast, the (111) mound decay is characterized by loss of atoms on all terrace levels producing a constant average slope. The mechanism for the decay on both surfaces at 297 K involves the diffusion of islands or terraces by periphery diffusion@footnote 2@ to an edge where a rapid decay@footnote 3@ or avalanche process may take place. Direct observation shows that this avalanche process is site selective on the (100) surface, but is not selective on the (111) surface. Kinetic Monte Carlo simulations@footnote 4@ at 400 K show that the observed behavior is a consequence of selective vs. non-selective edge diffusion barriers and does not depend on the mechanism by which atoms are delivered to the edge. @FootnoteText@ @footnote 1@ Supported in part by the U.S. DOE through contract DE-AC05-00OR22725 with UT-Battelle, LLC, and in part by the NSF of China. @footnote 2@ W. W. Pai, A. K. Swan, Z. Zhang, and J. F Wendelken, Phys. Rev. Lett. 79, 3210 (1997). @footnote 3@ M. Giesen, G. Schulze Icking-Konert, and H. Ibach, Phys. Rev. Lett. 80, 552 (1998). @footnote 4@ Maozhi Li, J. F. Wendelken, Bang-Gui Liu, E. G. Wang, and Zhenyu Zhang, Phys. Rev. Lett. 86, 2345 (2001).

11:40am **SS2-MoM7 Reactions on Free Platinum Clusters: Adsorption of Oxygen and Hydrogen and Formation of Water***, **M. Andersson**, A. Rosén,* Chalmers University of Technology and Göteborg University, Sweden

We use a cluster beam experiment to investigate chemical reactions on the surface of small unsupported metal clusters. A pulsed beam of metal clusters is generated with a laser vaporization source, in which metal atoms are vaporized into a flow of helium gas and condense in small clusters. After expansion into vacuum, the cluster beam passes through two reaction cells. The cell pressure is varied over a range where the clusters make from less than one up to a few collisions with the reactive molecules. The clusters are detected with laser ionization and time-of-flight mass spectrometry. By measuring the abundance of pure clusters and reaction products as a function of reaction cell pressure, the reaction probability in a cluster-molecule collision can be determined. For platinum clusters with more than 6 atoms we measure stable reaction products with both oxygen and hydrogen. The reaction probability with oxygen is for most sizes between 0.2 and 0.3, and appears lower with hydrogen though difficult to quantify since the Pt isotope distribution limits the mass resolution. If we let the clusters collide with both hydrogen and oxygen molecules, the resulting mass spectrum deviates significantly from a co-adsorption spectrum where the respective contributions are added. Instead, if, for example, the clusters first react with oxygen and then hydrogen we observe fewer oxide products and more pure clusters compared without hydrogen collisions. The only reasonable explanation for this is that water molecules are formed on the clusters and desorb. The efficiency of the reaction is high on all cluster sizes measured (8-30 atoms), with only a weak dependence on cluster size.

Thin Films
Room 123 - Session TF+MM-MoM
Thin Film Sensors

Moderator: D.L. Pappas, Duracell

10:20am **TF+MM-MoM3 MEMS Device Platforms as Research Tools for Developing Improved Sensing Films***, **C.J. Taylor**, S. Semancik, R.E. Cavicchi,* National Institute of Standards and Technology

Gas sensing characteristics of metal oxide films are dependent on the preparation method used in their fabrication. To optimize sensing film performance, one must understand how processing parameters influence composition and microstructure, and then correlate these changes with changes in the selectivity, sensitivity and stability of a sensor. We have been using arrays of microhotplates, MEMS devices fabricated with individually addressable heaters and sensing contacts, for both combinatorial studies and gas sensing. The short thermal time constant of the microhotplates makes them excellent microsubstrates for materials research where rapid heating and cooling during deposition are desired (heating rates of 10@super 5@ - 10@super 6@ °C /s are possible). Experiments have been performed using 4- and 16-element arrays as microsubstrates for CVD processing of titanium oxide and tin oxide using the single source precursors titanium(IV) nitrate, titanium(IV) isopropoxide and tin(IV) nitrate. Sensing films have been deposited both isothermally in the temperature range 100 to 450 °C, and using variable temperature deposition. Variable temperature deposition was achieved by applying triangle or square waves of varying frequency and amplitude to the heater. Film microstructure was examined by FESEM and its composition measured by EDS. We report on correlations between processing method, film microstructure and temperature dependent sensing performance for toluene, methanol, isopropanol, carbon monoxide, acetone, and other compounds.

10:40am **TF+MM-MoM4 Correlation Between Gas Response of MIS Field-Effect Sensors and the Bond Strength Between the Metal and the Insulator Layer of the Device***, **A.E. Åbom**, L. Hultman, M. Eriksson,* Linköping University, Sweden

Chemical gas sensors based on the field-effect are used in so called electronic noses as a powerful tool for various applications. The response mechanism is, however, not fully understood. In this work we monitor the material properties in order to understand the sensor properties. The sensors used in this work are Metal Insulator Semiconductor field-effect capacitors. The metal, Pt in this case, is grown by dc magnetron sputtering with varying growth parameters, with the Ar pressure ranging between 3 and 60 mTorr. The response to H@sub 2@ can be described by three steps,@footnote 1@ dissociation of H@sub 2@ molecules on the Pt surface, transport of H atoms through the Pt film and adsorption of H (at the metal-oxide interface) as polarized species (either as dipoles or as charged species). The polarized H affects the electric field as a shift in the applied voltage. This voltage shift increases with increasing hydrogen concentration in the ambient and reaches a saturation value depending on the amount of adsorption sites at the interface and on the magnitude of the polarization. We have found that the largest obtained voltage shift varies with the deposition process. The lower the saturation response is, the stronger the film is adhering to the substrate, as measured with e.g. scratch adhesion tests in a Hysitron TriboScope. From in-situ XPS studies it is found that no chemical reactions occur between Pt and SiO@sub 2@. We will discuss how the varying bond strength between the two materials is caused either by mechanical interlocking or electrostatic forces. We will further elaborate on whether the amount of adsorbed H at the interface changes between the different samples due to a varying electron density@footnote 2@ at the interface, or if the separation between the charges in the dipole layer is varying. @FootnoteText@ @footnote 1@ Lundström K.I., Shivaraman, M.S., Svensson, C.M., J. of Appl. Phys. 46(9) 1975 @footnote 2@ Norskov, J.K. Phys. Rev. B 26 (6) 1982.

11:00am **TF+MM-MoM5 On the Ammonia Response Mechanism of Field-effect Gas Sensors with Thin Pt Gates***, **M. Lofdahl**, M. Eriksson, I. Lundstrom,* Linköping University, Sweden

The ammonia sensitivity of Pt gate field-effect chemical sensors shows a strong dependence on the morphology of the thin metal gate. Several investigations have shown that thin Pt gates are necessary to achieve high ammonia sensitivity and that thick gates show a low or even no sensitivity to ammonia.@footnote 1,2,3@ Thin thickness means in this context that the Pt gate metal has to be made so thin that the underlying oxide is partly exposed. However, there exist an optimum, and if the thickness of the metal is made too thin the sensitivity decreases again. In this contribution the morphology of the thin Pt gate has been carefully investigated and characterised by SEM and complementary TEM studies and morphological parameters have been extracted for different processing conditions of the metal film deposition. By correlating the morphological parameters to measurements of the ammonia sensitivity in inert and oxygen-containing ambient the response mechanism is attributed to the existence of Pt-SiO2 boundaries in the metal. Further experimental investigations show that the Pt-SiO2 interfaces acts as catalytic sites for the dissociation of ammonia molecules and diffusion of detectable species from these sites determine the response. The diffusion length of the detectable species from the dissociation sites is strongly dependent on the existence of oxygen in the ambient. In an inert ambient the diffusion length can be several mm, whereas in 20 % of oxygen it is only in the order of mm. The most likely candidate for the detectable species is atomic hydrogen. @FootnoteText@ @footnote 1@ A. Spetz, M. Armgath, and I. Lundström, Journal of Applied Physics 63, 1274-1283 (1988). @footnote 2@ J. F. Ross, I. Robins, and B. C. Webb, Sensors and Actuators 11, 73 (1987). @footnote 3@ M. Löfdahl, C. Utaiwasin, A. Carlsson, I. Lundström, and M. Eriksson, Submitted to Sensors and Actuators B (2001).

11:20am **TF+MM-MoM6 Charge Transport Mechanisms in Epitaxial Tungsten Oxide Films Used for Chemiresistive Sensors***, **S.C. Moulzolf**, R.J. Lad,* University of Maine

Chemiresistive gas sensors fabricated from ultra-thin WO@sub 3@ films containing surface catalysts can be made highly sensitive towards a variety of target gases via manipulation of oxide surface chemistry. However, other important sensor characteristics including baseline stability, response time, and reproducibility are strongly dependent on the specific film microstructure and charge transport within the film. Using in situ Hall effect measurements coupled with structural analysis and gas testing experiments, we have determined a correlation between film deposition parameters, microstructure, and electrical response. WO@sub 3@ films were grown by rf magnetron sputtering on sapphire substrates to produce either epitaxial tetragonal or epitaxial monoclinic phases as deduced by RHEED and XRD. Exact film stoichiometries were controlled via post-deposition annealing treatments in vacuum and/or synthetic air environments. Four-point van der Pauw conductivity and Hall effect measurements as a function of temperature indicate that charge mobility is very small (<2cm@super2@V@super -1@s@super -1@) and that polaron hopping is the dominant conduction mechanism. The conductivity of the monoclinic phase is an order of magnitude larger than the tetragonal phase and exhibits temperature dependence similar to measurements from single crystal WO@sub 3@. The mobility of the tetragonal phase increases with temperature consistent with scattering from the increased number of grain boundaries and smaller grain size as observed by STM and XRD. Extended annealing in vacuum to reduce the oxide stoichiometry causes higher conductivity and temperature dependent mobility behavior that may be attributed to crystallographic shear plane defects in the WO@sub 3-x@ lattice. Upon gas exposure to H@sub 2@S or methanol, the tetragonal phase shows higher sensitivity compared to the monoclinic phase but a slower response which correlates with the lower Hall mobility.

Vacuum Science & Technology
Room 125 - Session VST-MoM

Sealed and Insulating Vacuum Systems

Moderator: M. Ferris, SAES Getters

9:40am **VST-MoM1 RHIC Insulating Vacuum System: Status and Performance@footnote *@***, R. Davis, H.C. Hseuh, D. Pate, L. Smart, **D. Weiss**,* Brookhaven National Laboratory

Superconducting magnets are used to bend and focus the heavy ions in Relativistic Heavy Ion Collider (RHIC), which has been operational for the past two years. The RHIC insulating vacuum systems consist of 40 large volumes and 112 smaller transfer lines with a cumulative length and volume over 10km and 2000 m@super 3@, respectively. Numerous pumps, valves, gauges and residual gas analyzers are deployed to maintain and monitor the integrity of the insulating vacuum, and thus minimize the heat transfer from the ambient cryostat wall to the magnet cold mass. The overall design, the construction, commissioning and operation experience of the RHIC insulating vacuum systems will be presented. The measurements and methods for locating internal helium leaks at various helium line temperatures and pressures will also be presented. @FootnoteText@ @footnote *@Work performed under the auspices of the U.S. Department of Energy.

10:00am **VST-MoM2 Getter Requirements for a CRT with a Diamond Coated FE Electron Source***, **V. Nemanic**, M. Zumer, B. Zajec,* ITPO, Institute of Surface Engineering and Optoelectronics, Slovenia*; T. Tyler,* North Carolina State University

A single diamond coated field emitter (FE) tip could be used as a replacement for the thermionic cathode in small electron beam devices offering better opto-electronic performance. The most important parameter limiting the use of field emitting sources is their short lifetime, which is closely related to the pressure level within the pinched off device. After the initial evacuation of the tube and bake-out, getter selection and the activation procedure would seem to play the crucial role. In the present study, the pressure of miniature CRTs was measured by a spinning rotor gauge (SRG) after the initial evacuation and bake-out procedures, again after activation of the getters, and finally during operation under typical operating conditions. Two commercial getter types were studied: Ba evaporable (St15/AM/O/9.5) and non-evaporable (NEG, St 172), made by SAES and built into the CRTs with either an oxide coated thermionic cathode or a diamond coated FE tip. The later were fabricated by electrochemically etching 125µm molybdenum wire in KOH, resulting in tips with radii of @<=@ 50nm. The bare tips were then coated with nanodiamond via electrophoresis using a 2g /L suspension of diamond in ethanol. After the evaporation of barium getters by the prescribed procedures, the pressure did not drop, but increased slowly from 1x10@super - 5@ mbar up to 1x10@super -3@ mbar, later shown to be methane. In CRTs with oxide cathode, getter pumping action could be triggered by switching on the cathode heater, which efficiently cracked the methane generated. In CRTs with a FE tip, there was no way to decrease the residual methane pressure to the desired level. The FE tips, previously approved and characterised in UHV, were thus irreversibly damaged ab initio. In CRTs with NEGs, no pressure increase was registered by the SRG during several days. This means that they can maintain the residual atmosphere at the level that may provide a long-term operation of devices with diamond coated FE electron sources.

10:40am **VST-MoM4 Applicability of Spinning Rotor Gauges to Pressure Measurements in Sealed System***, **J. Setina**, B. Erjavec, L. Belic,* Institute of Metals and Technology, Slovenia*; V. Nemanic,* ITPO, Slovenia

Spinning rotor gauge (SRG) is truly inert vacuum gauge and has remarkable resolution and long term stability. Measuring element is a small steel ball, which is kept inside a measuring thimble, while all other necessary elements for the gauge operation are kept outside vacuum. The measuring head easily decouples from the ball/thimble assembly and the volume of the thimble is only few ml. All this makes the gauge especially usable for pressure measurement in sealed systems. However the accuracy of pressure measurements in a sealed systems is affected by the gauge residual drag. The residual drag changes whenever the suspension head is removed but remains stable during the continuos suspension if the ball. This makes gauge more suitable for studying pressure changes in a sealed system than for absolute pressure measurements. Pressure changes in a sealed-off device can be caused by leaks and permeation, outgassing or gas pumping effects. Through the years we successfully used SRGs for studies of gas pressure in different sealed-of devices. We will describe our experience of using SRGs for measurements in image intensifiers, miniature cathode ray tubes and recently in channel electron photomultipliers, flat vacuum insulation panels, ultrasensitive leak detection and studies of hydrogen outgassing from stainless steel. We will discuss how the unknown gas composition in the sealed system and the ball-thimble geometry influences accuracy of the gauge in the transition from molecular to viscous regime.

11:00am **VST-MoM5 Sealed Vacuum Systems including Vacuum Insulation***, I.P. Della Porta,* SAES Getters SPA, Italy*; **L. Rosai**,* SAES Getters' Group Strategic Marketing Director **INVITED**

Vacuum systems can be continuously pumped discharging to air the gasses generated by the process or released by the internal surfaces. However an enormous number of vacuum devices after an initial processing and evacuation are insulated, and sealed-off. The maintenance of a good vacuum for long times requires both a sufficient pumping and efficient baking processes. In most cases an internal chemical pump, a getter, is used to take care of the gasses developed during these processes and the operations of the systems. Getter materials, getter pumps, ion-pumps, cryo-pumps are the most economical and efficient solutions. We will examine the requirements and the solutions of vacuum systems operating in the vacuum better then 1x10@super -10@ torr, typically particle accelerators; of applications where the required vacuum has to be better than 1x10@super -8@ torr, typically certain processes for the semiconductor industry; of devices in which the vacuum or the contaminants partial pressures are in the range of 1x10@super -2@- 1x10@super -8@ torr, typically electron tubes, displays (CRTs,FEDs,etc.) and lamps. We will examine also sealed off stainless steel devices like dewars or vacuum thermally insulated pipes with vacuum in the range of 1x10@super -6@ - 1x10@super -4@ torr. Finally, we will also consider a new generation of vacuum insulated panels for thermal insulation based on plastic materials where the vacuum is in the range of 1x10@super -3@ to 1 torr. We will illustrate the materials used, the treatments of the surfaces, the various types of tailor made getter materials for each group of vacuum systems. We will also mention the key factors and the mathematical models used to predict the vacuum evolution and the effects of the deterioration of vacuum on the working characteristics of the sealed- off devices.

Applied Surface Analysis
Room 134 - Session AS-MoA

Quantitative Analysis and Data Interpretation II: Electron Spectroscopies

Moderators: M.-G. Barthés-Labrousse, CNRS, France, J.E. Castle, University of Surrey, U.K.

2:00pm **AS-MoA1 Satellite Structure in the KLL Auger spectra of Ge***, **L. Kövér**, I. Cserny, J. Tóth, D. Varga, Z. Berényi,* Institute of Nuclear Research of the Hungarian Academy of Sciences, Hungary

Studying deep core Auger spectra in materials of practical interest is important for understanding solid state effects on Auger processes as well as for revealing the electronic structure of these systems, including localization and charge transfer. Very intense satellites were observed in the KLL Auger spectra of some 3d metals and alloys@footnote 1@ and in the LMM spectra of 4d metals@footnote 2@ in previous studies. An earlier work on the Ge KLL Auger spectra excited by Mo K@alpha@ radiation from a thin film of ca 10 nm thickness@footnote 3@ identified the presence of a strong satellite as due to the effect of inelastic electron scattering. Here we report the first high energy resolution measurements of the Ge KLL spectra. The spectra were excited by bremsstrahlung (using an X-ray source with Cu anode) from amorphous Ge overlayers of different, several ten nm thickness, deposited onto a Si substrate. Measurements of the KLL spectra were performed using a high energy hemispherical electron spectrometer.@footnote 4@ For identifying the nature of the satellite structure and the contributions from extrinsic and intrinsic processes, the spectra are compared to the corresponding energy loss spectra of backscattered electrons and the shape of the KLL spectra is analyzed using different models for inelastic background correction. This work was supported by the project OTKA T026514. @FootnoteText@ @footnote 1@ L. Kövér, Zs. Kovács, J. Tóth, I. Cserny, D. Varga, P. Weightman, S. Thurgate, Surface Sci. 433-435(1999)833. @footnote 2@ G.G. Kleiman, S.G.C. De Castro,R. Landers, Phys. Rev. B49(1994)2753. @footnote 3@ E. Sokolowski, C. Nordling, Arkiv för Fysik 14(1958)557. @footnote 4@ L. Kövér, D. Varga, I. Cserny, J. Tóth, K. Tökési, Surf. Interface Anal., 19(1992)9.

2:20pm **AS-MoA2 Optimized Analysis of Spectra: Application of Reciprocal-space Approaches to Broad, Sparse, and/or Multistructured Spectra***, **D.E. Aspnes**,* North Carolina State University*; S.D. Yoo,* Serome Ventures, Inc., Seoul, Korea

Using a procedure that we recently developed to remove endpoint-discontinuity artifacts in reciprocal-space (R-S) analysis of optical spectra, we solved the optimization problem for determining critical-point (CP) parameters for isolated structures and found that parameters such as CP energies could be obtained for a wide class of direct-space lineshapes even if the lineshapes were not known a priori.@footnote 1@ Here, we extend this work to the analysis of spectra that contain structures that are broad, such as those encountered in photoemission, that are sparse (those that are represented by only a few data points), such as Raman spectra obtained with array detectors, or that contain a multiplicity of CP structures, such as those encountered in optical spectra at higher energies. For the multiple-CP case the advantages of R-S analysis are retained. We obtain a simple expression that describes the effect of overlayers on the CP energies obtained from optical spectra. For sparse spectra and those containing broad structures R-S analysis shows, not surprisingly, that the information content is low and the most efficient approach appears to be to assume a lineshape and perform curvefitting in direct space as is currently done. Extensions of the approach to two or more dimensions, of interest to image processing, are also discussed. @FootnoteText@ @footnote 1@S. D. Yoo and D. E. Aspnes, J. Appl. Phys. (in press).

2:40pm **AS-MoA3 Quantitative AES and XPS - Databases Test Quantification Validity***, **M.P. Seah**, I.S. Gilmore, S.J. Spencer,* National Physical Laboratory, UK

For quantitative analysis by AES and XPS we may either use theoretical or experimental sensitivity factors (SFs). In the past, many analysts have used experimental SFs deduced from data for pure elements or have calculated such data. Both of these will lead to erroneous results. It is shown that the correct SFs for analysing homogeneous mixtures are those deduced for a common, or average, matrix.@footnote 1@ These may be calculated according to easily defined rules.@footnote 1,2@ Experimental SFs from NPL databases for AES and XPS agree closely with theory apart from one factor that varies from element to element but is the same for AES as for XPS and is independent of the electron emission energy. This factor is attributed to an inadequacy either of the background subtraction method for the experimental peak areas or of the material-to-material dependence of the inelastic mean free path (IMFP) for the theory. A number of improvements have been made in the background subtraction method which now uses data from an angle-averaged REELS database@footnote 3@ instead of the Tougaard method. The background subtracted XPS spectra have intrinsic loss intensities that are consistent with theoretical predictions. Analyses show that the main error may come from the material-to-material dependence of the IMFP but that the new average matrix sensitivity factors avoid this error. Apart from the single factor for each element, which is the same for AES as for XPS, the correlations between experiment and theory exhibit scatters of 8% and 11% for AES and XPS, respectively. These correlations are shown to be valid in AES for K, L, M or N shell Auger electron peaks with kinetic energies above 180 eV and in XPS for all shells except the weak s shells for Z > 20. @FootnoteText@ @footnote 1@M P Seah and I S Gilmore, Surf. Interface Anal. 26(1998)908. @footnote 2@M P Seah, I S Gilmore and S J Spencer, J. Elec. Spectrosc. to be published. @footnote 3@M P Seah, Surf. Sci. 471(2001)782.

3:00pm **AS-MoA4 Surface Excitations of Medium Energy Electrons in Metals and Semiconductors***, **W.S.M. Werner**, W. Smekal, C. Tomastik, H. Stoeri,* Vienna University of Technology, Austria

Reflection energy electron loss spectra (REELS) have been measured for several metals and semiconductors (Be, Al, Si, V, Fe, Co, Ni, Cu, Ge, Mo, Pd, Te, Ta, W, Au, Pb) in the medium energy range (150-3400 eV) for normal incidence and an emission direction of 60 with respect to the surface normal. The ratio of the number of electrons that induced a surface excitation to the intensity of the elastic peak was extracted from each spectrum providing the total surface excitation probability (SEP). For the nearly free electron materials the results agree reasonably with free electron theory while significant deviations are observed for the other materials. In all cases the SEP is proportional to the time the probing electron spends in the vicinity of the surface. It is generally found that the surface excitation probability decreases with the generalized plasmon energy. A simple predictive formula to estimate the surface excitation probability for medium energy electrons entering or leaving an arbitrary material is proposed.

3:20pm **AS-MoA5 The Attenuation Length Revisited***, **A. Jablonski**,* Polish Academy of Sciences, Poland*; C.J. Powell,* National Institute of Standards and Technology

The attenuation length, and the preferred replacement term effective attenuation length (EAL), have been a source of confusion in surface analysis by Auger-electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). The EAL is formally defined in terms of the local slope of the emission depth distribution function (EDDF). This definition is relevant to the determination of the depth of a thin marker layer. The EAL is also frequently used as a term to determine the thicknesses of thin overlayer films from measurements of AES or XPS signal intensities. We show that while the formal EAL definition does not correspond conceptually to this important application, numerical EAL values calculated from changes of signal intensities are similar to values obtained from the formal EAL definition for some experimental configurations. The EALs for the marker-layer and overlayer-film applications are what we term "local" EALs since they were derived from the reasonable assumption that the EDDF could be regarded as an exponential function of marker depth or overlayer-film thickness for small ranges of depths or thicknesses. We point out that it is also useful to define "practical" EALs for a wider range of depths or thicknesses. We have made calculations of local and practical EALs for XPS with Mg K@alpha@ X-rays in a range of measurement configurations for Si 2s photoelectrons in Si (for which elastic-electron scattering effects are relatively weak) and for Au 4s photoelectrons in Au (for which the elastic-scattering effects are relatively strong). In general, the local and practical EALs for each solid vary with the measurement conditions. Nevertheless, the practical EALs for overlayer- film thickness measurements in conventional XPS experiments do not vary appreciably with emission angle for emission angles between 0 deg and about 65 deg with respect to the surface normal. A similar result was found for three Auger transitions in Au.

3:40pm **AS-MoA6 Comparisons of Practical Effective Attenuation Lengths and Inelastic Mean Free Paths for Applications in AES and XPS***, **C.J. Powell**,* National Institute of Standards and Technology*; A. Jablonski,* Polish Academy of Sciences, Poland

The practical effective attenuation length (EAL), defined in terms of changes in signal-electron intensities, is needed (as the "lambda parameter") for measurements of overlayer thicknesses by AES and

XPS.@footnote 1@ We have calculated practical EALs for principal photoelectron and Auger-electron lines in Si, Cu, Ag, and W using an algorithm based on solution of the kinetic Boltzmann equation within the transport approximation.@footnote 2@ These calculations were made for values of the angle of emission @alpha@ between 0 and 80° and, for XPS, a configuration in which the angle between the x-ray source and the analyzer axis was 55°. For @alpha@ < 60°, the ratio of the practical EAL to the corresponding inelastic mean free path (IMFP) is nearly constant with emission angle, and varies in magnitude between 0.68 and 0.91. The deviation of this ratio from unity is due to the effects of elastic-electron scattering. We find that the ratio varies approximately linearly as a function of the single-scattering albedo that is defined in terms of the IMFP and the transport mean free path (TMFP). While the albedo varies in a complicated manner with atomic number and electron energy, it provides a convenient measure of the effects of elastic-electron scattering. For @alpha@ > 60°, the ratio of the practical EAL to the IMFP increases rapidly with emission angle. At these more grazing emission angles, practical EALs should be determined for the specific film thicknesses and emission angles of interest in order to obtain reliable measurements of film thicknesses. @FootnoteText@ @footnote 1@A. Jablonski and C. J. Powell (to be published). @footnote 2@I. S. Tilinin, J. Zemek, and S. Hucek, Surf. Interface Anal. 25, 683 (1997).

4:00pm **AS-MoA7 Surface Analysis of Hafnium Compounds by XPS using High Energy Zr Source**, ***P. Mrozek**, D.F. Allgeyer, B. Vaartstra,* Micron Technology, Inc.

The deep 3d5/2 core level at Eb = 1662 eV of Hf in a metallic state, as HfO2, and as HfSi2 were investigated by X - ray photoemission using the Zr LÎ± source. The study was undertaken for the sake of quantitative analysis of hafnium thin films used as common diffusion barriers.@footnote 1@ Chemical shifts of Hf 3d5/2 were determined together with Auger parameter values for M3N6,7N6,7 (Ek = 1615 eV) Auger electron transition and used to probe the evolution of chemical bonding in hafnium films. The effect of initial state from the configuration interaction within the Hf 4f shell onto the quantitative analysis was examined. Common spectral overlaps of the Auger electron and photoelectron lines in hafnium compounds were discussed. @FootnoteText@ @footnote 1@Ken-ichi Yoshimoto, Satoko Shinkai, Katsutaka Sasaki, Jpn. J. Appl. Phys. 39 (2000) 1835.

4:20pm **AS-MoA8 VAMAS TWA2 Project A2, Evaluation of Static Charge Stabilization and Determination Methods in XPS on Non-conducting Samples: Report on an Inter-laboratory Comparison**, ***W.E.S. Unger**, Th. Gross, O. Boese, A. Lippitz, Th. Fritz,* Bundesanstalt fuer Materialforschung und -pruefung (BAM), Germany; *U. Gelius,* Uppsala Universitet, Sweden

Results of an inter-laboratory comparison (27 participants in Europe, Japan and USA) of XPS data obtained with non-conductive samples are presented. Binding energies of Al 2s for alumina, N 1s and imide C 1s for Kapton and Sr 3p3/2 for a strontium titanate film on glass were obtained after static charge referencing with the help of 15 nm gold particles deposited at the surface of the test samples. For the alumina sample C 1s static charge referenced data are presented, too. In any case repeat standard deviations, between standard deviations, reproducibility standard deviations and total means are evaluated from the experimental data. It can be stated, that though the repeat standard deviation is small as 0.05 eV in the best case, the standard devia-tion characterizing the reproducibility of the method is obviously not better than 0.15 eV, also in the best case, at the present time. The knowledge of these standard deviations is important for metrology, validations of analytical procedures relying on qualitative photoelectron spectroscopy and XPS databanking.

4:40pm **AS-MoA9 Real and Gedanken Experiments Related to Surface Charging during XPS Measurements of Insulating Materials and Thin Films**, ***D.R. Baer**, M.H. Engelhard, Y. Liang, A.S. Lea, D.J. Gaspar, C.F. Windisch,* Pacific Northwest National Laboratory

The ability to accurately obtain binding energy measurements can be important for interpretation of XPS data for many different applications. In recent studies of thin oxidized aluminum layers we have seen a range of phenomena that both confound easy data analysis and provide opportunities to learn critical information about oxide layers. In this paper, we will examine the binding energies obtained from oxidized aluminum formed in aqueous solutions and transferred to vacuum without exposure to air. Data from pure aluminum and copper containing aluminum alloys will be compared with each other and to other data in the literature. Influence of ion and electron bombardment and oxide doping will be presented. A more general examination of some issues related to understanding binding energies from oxides and oxide films will be discussed. A summary of some physical phenomena that occur during XPS measurements of thin insulating layers on conducting or semi-conducting substrates that can complicate charge referencing will be given. Some classic experiments of grounded and ungrounded specimens will be reported for a new generation of instruments with advanced methods of charge control and illustrative data from other systems will be reported.

5:00pm **AS-MoA10 Core-level Photoemission of Zirconium and Hafnium Silicates for Use as High Dielectric Oxides**, ***R.L. Opila**, R.B. Van Dover, G.D. Wilk,* Agere Systems

Photoelectron spectroscopy is often used to characterize the composition and bonding in high dielectric constant materials being developed for the next generation of integrated circuits. However, the peak positions vary continuously as a function of composition and thickness for binary oxides. Thus we have studied the core-level photoemission spectra of hafnium silicates and zirconium silicates, sputter deposited on silicon, as a function of oxide thickness. The metal peak shifts by as much as 1 eV to higher energy as the silicate component is increased. The Si 2p peak also shifts to greater binding energy as silicate component is increased. For pure metal oxide, the O 1s shows two components corresponding to the hydroxide and oxide at higher and lower binding energies respectively. As the silicate component is increased a new component appears at even higher binding energy. In addition to all of these peak shifts, for a given composition, a thin layer (less than 10 nm) has lower binding energies than seen for a corresponding thick film. All of these shifts in metal core-level, Si 2p, and O 1s can be related to two phenomena. The first is the relative electron donation of the metal and Si. Since the metal easily donates its valence electrons to oxygen, the O 1s peak is found at lower binding energies. As the Si component is increased, less electron density is donated to the oxygen, shifting the O 1s to greater binding energies. The oxygen then withdraws slightly more electron density from the metal, shifting its core levels to high binding energy. This reasoning can be used to explain all of the peak shifts seen for a given thickness. Thin films have lower binding energy because electrons near the Fermi energy help screen the positively-charged photoemission final state. This effect has also been seen for thin silicon dioxide films grown on silicon.

Biomaterials

Room 102 - Session BI+SS-MoA

Role of Water in Biological Systems

2:00pm **BI+SS-MoA1 Simulation Studies of the Structure and Dynamics of Biological Hydration Water**, ***D.J. Tobias,*** University of California, Irvine*; M. Tarek,* National Institute of Standards and Technology **INVITED**

Water, life's solvent, plays two vital roles in the function of biological macromolecules and their assemblies. One is to stabilize the specific structures that these molecules maintain in their functioning states. Another is that fast movement of water molecules promotes the flexibility of biological molecules required for their function. I will present results from molecular dynamics simulations that illustrate two peculiar aspects of water structure and dynamics near biological molecules. The first is the structure of water on the surface of lipid membranes. I will show that the first layer of water coating the membrane surface is strongly influenced by the lipid molecules, and that the anisotropic solvation of the lipid polar groups profoundly affects the polarity of the membrane/water interface. The second is the motion of water molecules on the surface of proteins. Below a threshold level of hydration and thermal energy, proteins exist in an inactive, glassy state. I will show that the transition from the glassy state to the functioning state requires relaxation of the protein-water hydrogen bond network. Finally, I will discuss some of the anomalous dynamical properties of protein hydration water, drawing analogies with supercooled and confined water.

2:40pm **BI+SS-MoA3 Local Solvation Shell Measurement in Water using a Carbon Nanotube Probe**, ***S.P. Jarvis,*** Nanotechnology Research Institute, AIST, Japan*; T. Ishida,* Institute for Mechanical System Engineering, AIST, Japan*; C.C. Liew,* Research Institute for Computational Sciences, AIST, Japan*; H. Tokumoto,* Nanotechnology Research Institute, AIST, Japan., Japan*; Y. Nakayama,* Osaka Prefecture University, Japan **INVITED**

Using a multiwalled carbon nanotube as an atomic force microscope (AFM) probe tip we have directly measured localised structuring in aqueous environments at small tip-sample separations and have combined this with nanometer resolution images of the surface. By diversifying beyond the simple surfaces of graphite and mica, to self-assembled monolayers with varying end groups, we have been able to investigate the role of local surface chemistry and morphology on the measured water structure. Directly measuring solvation shells with a mechanical probe of lateral dimensions comparable to that of a single molecule provides an invaluable insight into the processes controlling if and how a molecule approaches another molecule or a membrane. In the immediate vicinity of the molecule, continuum models break down and the aqueous environment will often form a discrete layered structure depending on the nature of the molecule. The absence or presence of such structure may be fundamental in influencing the promotion or inhibition of protein adsorption, biological function and membrane recognition. In order to perform such measurements it has been necessary to combine a number of innovative techniques with a standard AFM. For high-resolution imaging we use a highly sensitive frequency modulation detection scheme. To do this effectively in liquid involves the implementation of magnetically activated dynamic mode (MAD-mode!) where a small magnetic particle is attached to the end of the cantilever and an external magnetic field applied via a current carrying coil. To increase the sensitivity of the measurement to the interaction local to the tip apex we have used a high aspect ratio multiwalled carbon nanotube probe. This reduces the hydrodynamic squeeze damping between the surface and the bulk of the tip. The nanotube is attached in a specially designed field emission scanning electron microscope, which permits us some control over both the length and direction of the probe.

3:20pm **BI+SS-MoA5 The Role of Interphase Water in Protein Resistance***,* ***J.G. Kushmerick****, J.E. Houston, B.C. Bunker,* Sandia National Laboratories

While the inertness of oligo(ethylene glycol) (OEG) terminated self-assembled monolayers (SAMs) towards protein adsorption is well documented, the physical cause for the protein resistance has remained the subject of debate. Steric repulsion, which accounts for the inertness of endgrafted poly(ethylene glycol), is not applicable to thin densely packed OEG-SAMs. A strongly bound water layer templated by the OEG-SAM has been proposed to account for the protein resistance. Interfacial force microscope measurements of the interaction between functionalized probe tips and OEG-SAMs in water reveal a long-range (> 4 nm) repulsion. The repulsion is consistent with the existence of a thick interphase water layer with an elastic modulus similar to that of ice. Such an interphase layer, which is consistent with theoretical calculations and neutron reflectivity data, could account for the protein resistance of OEG-SAMs. Experiments aimed to further understand the mechanical properties of the water interphase, including varying the metal substrate, variable temperature and quartz crystal microbalance measurements, will also be discussed. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the US Department of Energy.

3:40pm **BI+SS-MoA6 Computer Simulation of the Behavior of Water near Model Surfaces and Self-Assembled Monolayers***,* ***A.J. Pertsin****, T. Hayashi, M. Grunze,* Heidelberg Universität, Germany **INVITED**

The Grand canonical ensemble Monte Carlo technique is used to simulate the behavior of the TIP4P model of water confined between two parallel hydrophilic or hydrophobic model surfaces and also the surfaces of oligo(ethylene oxide) (EGn) terminated self-assembled monolayers (SAMs). The interaction of water with hydrophobic surfaces is modelled by a conventional (3-9) potential dependent only on the separation of the water oxygen atom from the surface. The model potential for hydrophilic surfaces involves in addition an orientation dependence of the potential well depth, which allows for the orientation of the water hydrogens and lone pairs with respect to the proton-acceptor and/or proton-donor centers on the model surface. The water-SAM interactions are described using an atomistic force field based on ab initio MP2 level results for small EGn-water complexes.@footnote 1@ The transferability of the force field on the particular EGn chains constituting the SAM is tested by comparing the force field predictions with the relevant ab initio DFT results.@footnote 2@ The effect of the surfaces on the contiguous water is analyzed in terms of hydration pressure, average water density, and various distribution functions characterizing the orientational and positional order in water. The simulated water density distribution near the SAM is in good agreement with recent neutron reflectivity measurements which reveal the existence of a fairly thick (c.a. 50 Å) interphase water layer with a noticeably reduced average water density (85-90 % bulk water density).@footnote 3@ @FootnoteText@ @footnote 1@ D. Bedrov, M. Pekny, G. D. Smith, J. Phys. Chem. B 102, 996 (1998). @footnote 2@ R. L. C. Wang, H. J. Kreuzer, M. Grunze, Phys. Chem. Chem. Phys. 2, 3613 (2000). @footnote 3@ D. Schwendel et al., submitted.

4:20pm **BI+SS-MoA8 The Water Content of Proteins during Adsorption***,* ***J. Voros****, M. Textor, N.D. Spencer,* ETH-Zurich, Switzerland

Adsorption of proteins at solid-liquid interfaces is a process of central importance for biosensors and biomaterials. The role of water is a key issue in this process. The use of two biosensor techniques and identical experimental conditions have made it possible to follow the evolution of the water content of proteins during the surface adsorption-relaxation process.@footnote 1@ Optical waveguide lightmode spectroscopy (OWLS) involves the incoupling of a laser into a planar waveguide generating an evanescent field. The measurement of the incoupling angles allows for the online monitoring of the dry mass of surface-adsorbed macromolecules. Quartz crystal microbalance with dissipation factor (QCM-D) is a technique for monitoring the mass of adsorbed molecules via changes in the resonant frequency, f, while also getting information about the viscoelasticity of the layer by measuring the dissipation factor, D. The f-shift of the QCM-D is due to the change in total coupled mass, including the water coupled to the layer. The amount of water in an adsorbed adlayer can thus be determined by subtracting the adsorbed mass value obtained by OWLS from the value measured by the QCM-D in experiments carried out under identical conditions. The water content of the protein layer was found to be characteristic for different proteins and to change during the adsorption process. The time evolution of the water content provides information on the conformational changes during the adsorption. The dissipation factor measured by the QCM-D correlates well with the amount of water present in the adsorbed protein layer. Several blood proteins were measured on hydrophilic (TiO@sub 2@) and on hydrophobic surfaces. Dependence on the protein concentration and on the ionic strength of the buffer was also examined. @FootnoteText@ @footnote 1@ F. Hook, J. Voros, M. Rodahl, R. Kurrat, P. Boni, J.J. Ramsden, M. Textor, N.D. Spencer, P. Tengvall, J. Gold, B. Kasemo, Colloids and Surfaces B: submitted, 2000.

4:40pm **BI+SS-MoA9 X-Ray Absorption Spectroscopy of Liquid and Gaseous Water***,* ***K.R. Wilson****, R.J. Saykally,* University of California-Berkeley*; J.G. Tobin,* Lawrence Livermore National Laboratory

X-ray absorption fine structure (XAFS) measurements have been performed upon liquid@footnote 1@ and gaseous@footnote 2@ H2O. Using the O1s level as the means of achieving elemental specificity, both near edge (NEXAFS) and extended X-ray absorption fine structure (EXAFS) have been measured. Liquid water samples were achieved in the vacuum system via the utilization of a liquid jet system modelled after that of Faubel et al.@footnote 3@ In the investigation of liquid water, both ions and electrons were used as a means of detection. This permitted the separation of liquid surface effects (ions) from bulk-like behavior (electrons). In the NEXAFS regime, the surface sensitive spectrum resembled that of gaseous water while the bulk-sensitive spectrum exhibited broadening and a blue shift. Similarly, differences were observed in the EXAFS results derived from each detection method, i.e. surface vs. bulk. The measurement of the EXAFS in liquid water encouraged us to go back and perform similar measurements upon gaseous water. A single oscillation was observed from gaseous water consistent with the location of the covalently bonded hydrogen in H2O. The experimental phase and amplitude of the oscillation are in excellent agreement with curved wave multiple scattering calculations for isolated water molecules, performed by Ankudinov and Rehr.@footnote 2@ With this determination of the O-H scattering phase shift , the covalent hydrogen bond distance (0.95 + 0.03 Ã…) in liquid water has been quantified, thus demonstrating that hydrogen EXAFS can become a valuable complement to existing structural methods in chemistry and biology. @FootnoteText@ @footnote 1@K. R. Wilson, et al, J. Chem. Phys. B, May 2001. @footnote 2@K. R. Wilson, et al, Phys. Rev. Lett. 85,4289 (2000). @footnote 3@M. Faubel et al, J.Chem. Phys. 106, 9013 (1997).

5:00pm **BI+SS-MoA10 Proton Dynamics in Ice: A Resonant Photoemission Study***,* ***D. Nordlund****,* Uppsala University, Sweden*; M. Cavalleri,* University of Stockholm, Sweden*; H. Ogasawara, L.-Å. Näslund, M. Nagasono,* Uppsala University, Sweden*; L.G.M. Petterson,* University of Stockholm, Sweden*; A. Nilsson,* Uppsala University, Sweden and Stanford University, Sweden

We have studied resonant photoemission around the O-K edge of ice. There is an interference effect between the direct photoemission and core decay processes seen in the valence orbitals. The most striking results is a binding energy shift of 0.5-1 eV of the valence states upon excitation into a core exciton at the bottom of the conduction band in ice. The shift in the orbital energies can be related to motions of the proton to the neighbouring water molecule connected through a donor H-bond during the lifetime of the core hole. This will give us a probe to study proton dynamics in H-bonded system on a femtosecond time scale. We are currently computing the potential of the proton in the core-excited state using DFT.

Dielectrics
Room 130 - Session DI-MoA
High K Dielectrics I

Moderator: M.A. Leskela, University of Helsinki, Finland

2:00pm **DI-MoA1 Epitaxial High-K Gate Oxides on Silicon: Impact on Future CMOS**, ***Z. Yu***, *R. Droopad, J. Ramdani, J. Curless, C. Overgaard, J. Finder, K. Eisenbeiser, J. Wang, W. Ooms,* Motorola Labs; *Y. Liang, S.A. Chambers,* Pacific Northwest National Laboratory **INVITED**

One of the main problems facing the semiconductor industry is the scaling of the gate dielectric of silicon CMOS devices. Currently, SiO@sub 2@ gate oxide is being used, but it suffers from tunneling leakage current and reliability problems at thickness below 2 nm. Alternative high-k materials to replace SiO@sub 2@ need to be developed as soon as possible. Single crystal oxides such as SrTiO@sub 3@ (STO) with a simple structure and a much higher k are ideal candidates for future CMOS gate dielectrics. A physically thick high-k layer can behave electrically like a thin one, thereby eliminating the tunneling leakage problems experienced with <2 nm SiO@sub 2@. These oxides also exhibit ferroelectric behavior and their use as the gate dielectric on Si can be exploited in the realization of a single transistor memory element. In this presentation, we will review the atomic simulation, MBE growth, structural, electrical and interface properties of high quality single crystal STO layers on Si with low leakage current density and effective oxide thickness (EOT) < 1 nm. The STO layers are characterized using RHEED, SE, XRD, AFM, TEM and XPS. Atomic simulations have been extensively carried out to predict the reliability of the structure of the epi-oxide/Si interface. The oxide films on Si(001) are (001) orientated as determined by XRD and pole figure analysis confirms that the perovskite oxide lattice is rotated 45° with respect to the Si lattice. AFM measurements shows rms roughness as low as 1.2 Å. Cross-sectional TEM shows smooth interfaces and dislocation free STO films. XPS has been used to determine the band offsets at the oxide/Si interface. Electrical measurements on MOS capacitors fabricated on wafer using platinum gate electrodes demonstrated leakage as low as 10@super -8@ A/cm@super 2@ with interface state densities in the low 10@super -11@ cm@super -2@eV@super -1@. Results on MOSFET devices fabricated using STO as the gate insulator will be presented.

2:40pm **DI-MoA3 High Dielectric Constant Material as an Alternative Gate Dielectric in MOSCAP and MOSFET Applications**, ***Y.S. Lin***, *J.P. Chang,* University of California, Los Angeles

ZrO@sub 2@ is investigated in this study to replace SiO@sub 2@ as the gate dielectric material in metal-oxide-semiconductor devices. ZrO@sub 2@ films were deposited on P-type Si (100) wafers by a rapid thermal chemical vapor deposition process using Zr(OC@sub 4@H@sub 9@)@sub 4@ as the precursor and oxygen as the oxidant. The two chemistries were introduced sequentially into the reactor with purging and evacuation in between. The deposited films were stoichiometric, uniform and extremely smooth based on X-ray photoemission, ellipsometry, and atomic force microscopy measurements. The high-resolution transmission electron micrograph showed a polycrystalline ZrO@sub 2@ film (monoclinic) and an interfacial amorphous ZrSi@sub x@O@sub y@ layer on the silicon substrate. This interfacial layer is confirmed to be zirconium silicate based on the thermodynamic calculation, chemical etching resistance, and medium energy ion scattering analysis. Excellent step coverage was observed by depositing ZrO@sub 2@ over 300 nm features with an aspect ratio of 4. The conformal deposition profile can be simulated by the Monte Carlo method with a sticking coefficient on the order of 10@super -4@. In-situ transmission infrared analysis is used to examine the chemically absorbed surface species during the deposition process with various chemical exposures. Isotope labeling of oxygen is underway to assess the effect of the oxidation/annealing processes on film composition and electrical performance. The dielectric constant of RT-CVD ZrO@sub 2@ was 15-18, and the capacitance-voltage measurement showed a hysteresis around 100 mV, which was slightly higher than desired <45 mV value. The interface state density was ~ 1.2x10@super 11@ cm@super -2@eV@super -1@, as determined by capacitance measure at various frequencies. NMOS transistors are made with n@super +@ polysilicon gate, and good turn-on characteristic and low leakage current density of 2x10@super -7@ A/cm@super 2@ at - 1.5V were observed.

3:00pm **DI-MoA4 High Frequency Characterization of Thin Films with High Dielectric Constant**, ***J. Westlinder***, *K. Larsson, H.-O. Blom, J. Olsson,* Uppsala University, Sweden

New dielectric materials are required in future IC's. Not only a new gate oxide with higher dielectric constant is needed, but also high dielectric materials must be used in on-chip integrated capacitors in order to increase the integration density. We have investigated the high frequency behavior of (Metal-Insulator-Metal) MIM-capacitors in the frequency range from 1 MHz to 10 GHz. The insulator thin films (about 100 Å to 2000 Å) have been made of high dielectric constant materials, e.g. Ta@sub 2@O@sub 5@, ZrO@sub 2@, or HfO@sub 2@. In the tantalum oxide case, there seems to be a dependence in dielectric constant with frequency. At higher frequencies (over about 1 GHz) there is a rapid decrease in the dielectric constant due to relaxation effects. A first order equivalent circuit model has been developed and simulated, showing good agreement with the measurements. Also, the results show a decrease in dielectric constant with decreasing thickness of the films. These preliminary results indicate that the performance of RF-devices and RF-circuits might be seriously degraded in the GHz region. In addition, the DC I-V characteristics were measured in terms of leakage current density and breakdown voltage, and will be presented.

3:40pm **DI-MoA6 Interfacial Stability of High-k Dielectrics Deposited by Atomic Layer Chemical Vapor Deposition**, ***W. Tsai***, IMEC (Intel assignee), Belgium; *H. Nohira, R. Carter, M. Caymax, T. Conard, S. De Gendt, M.M. Heyns, J. Petry, O. Richard, W. Vandervorst, E. Young, C. Zhao,* IMEC, Belgium; *J. Maes,* ASM Europe, The Netherlands; *M. Tuominen,* ASM Europe, The Netherlands, Belgium

Control of interfacial oxide growth is critical to achieving sub 1 nm Equivalent Oxide Thickness in high k gate stacks for future generations microelectronic devices. The formation of interfacial oxide is dependent on Si surface preparations, high k dielectrics deposition, post deposition conditioning such as thermal anneal and air exposure. In this work, effect of various interfaces on initial growth of high k layers, interface stability and electrical peformance were investigated. High-k dielectrics layers are grown by Atomic Layer Chemical Vapor Deposition (ALCVD), dielectrics and interfacial layer thickness /composition were characterized by X-ray Fluorescence, X-ray Photoelectron Spectroscopy (XPS) and Transmission Electron Microscopy (TEM). An initial high k dielectrics layer formation with inhibited growth was observed for both ALCVD Al2O3 and ZrO2 films, followed by a linear growth regime with a full coverage layer. For high k dielectrics deposited on Si substrates with hydrogen termination from HF dip, growth of interfacial oxide SiOx was quantified as a function of air exposure. Interfacial oxide forms due to oxygen permeation through the high k layers, either during air exposure; during thermal anneal in an oxygen ambient (>500oC) or during the ALCVD growth itself whereby the growth process itself acts as an oxygen source. The latter is observed in the case of ZrO2 where the interfacial oxide scales with ZrO2 layer thickness. In addition, an intrinsic interfacial oxide growth is observed with XPS from as-deposited high k dielectrics films. For Al2O3, an interfacial oxide of approx. 1.5 Ã… for thickness > 2 nm, reflecting the possible formation of Al-O-Si bond. Minimization of interfacial oxide growth in high k gate stacks was demonstrated with an in-situ poly-silicon cap on Al2O3 to restrict the oxygen diffusion. The stability of such capped high k/ Si interface was also shown to be intact after 1000oC RTP anneal in nitrogen.

4:00pm **DI-MoA7 First Step Towards Crystalline Titanate-Si Integration: Formation of Atomic Layer Strontium Silicate on Si(001)**, ***S. Gan***, *Y. Liang, S. Shutthanandan, S. Thevuthasan,* Pacific Northwest National Laboratory

Recent work showed that crystalline titanates grown on Si(001) exhibited promising properties as the potential high-K gate oxides for CMOS. One of the critical issues in this approach is the interfacial template layer that needs to possess favorable struc tural and chemical properties for growth of crystalline oxides on Si. We present our recent results on the study of the initial stage of oxide growth on Si(001). Using scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), and Rutherford back scattering (RBS), we investigated the structural and chemical behaviors of six strontium based templates grown on Si. It was found that depending on the surface strontium coverage, the strontium-covered Si surfaces exhibit a series of reconstructions. These reconstructions not only had different atomic structures but also different stability against oxidation and the oxide growth. For instance, upon exposure to oxygen, the (3x2) reconstruction was converte d to a disordered (1x1) surface while the Sr/Si-(1x2) reconstruction remained intact. For the growth of oxides, the (1x2) structure was found to provide the most stable interface, as evidenced by a uniform layer in angular dependence XPS results, the lack of interfacial SiO@sub2@ layer, and the ability to form single-crystal SrO films on this structure. By combining results obtained from STM, XPS, RBS, and LEED, we correlated the interface structures with film properties, which allowed us to identify suitable interfacial templates for optimized growth of titanates. @FootnoteText@ Pacific Northwest Laboratory is a multiprogram national laboratory operated for the U.S. Department of energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.a.

4:20pm **DI-MoA8 High-k Metal Oxide Dielectrics Deposited by CVD using Oxygen and Ozone***, **M. Yoon**, V.K. Medvedev, K.D. Hauch,* University of Washington*; J.W. Rogers, Jr.,* Pacific Northwest National Laboratory*; Y. Ono, S.T. Hsu,* Sharp Laboratories of America

TiO@sub 2@ thin films have generated considerable interest in high-k gate oxide applications. Previously we have described a novel process for creating high purity, carbon-free TiO@sub 2@ films on Si utilizing a TiO@sub x@ buffer layer.@footnote 1@ Here, improvements in oxidizing this buffering Ti layer using ozone (O@sub 3@) are presented. Auger electron spectroscopy (AES) analysis show similar stoichiometry of Ti and O when using either oxygen or ozone at room temperature. Low energy electron diffraction (LEED) analysis was conducted on Si, Ti/Si, and O@sub 2@ oxidized Ti/Si. Preliminary results show: an initial Si substrate with a highly ordered 2x1 structure prior to the deposition of Ti, a crystalline Ti film deposited on the Si, and the amorphorization of the Ti after oxidation with O@sub 2@. It is our aim to produce an amorphous TiO@sub 2@ film on the TiO@sub x@ buffer layer and thus the amorphous structure of this buffer layer is desired. Oxygen deficiency in TiO@sub 2@ gate oxide films is a major cause of increased leakage current. O@sub 3@ is an attractive alternative to O@sub 2@ as an oxidizer since it produces atomic oxygen (O) upon decomposition which can react with single dangling bond sites on the film surface, and thus create a denser, oxygen rich film. The co-deposition of the titanium isopropoxide (TTIP) precursor with O@sub 3@ for creating a CVD-TiO@sub 2@ film on the buffer layer has been compared to the co-deposition of TTIP with O@sub 2@. AES and electron spectroscopy for chemical analysis (ESCA) measurements show few compositional differences between the two TiO@sub 2@ films, however, atomic force microscopy reveals distinctly different morphology. The application of TiO@sub 2@ and other similarly produced metal oxide films (e.g. HfO@sub 2@) as gate oxides in MOS devices is also being explored. @FootnoteText@ @footnote 1@A. Tuan, M. Yoon, V. Medvedev, Y. Ono, Y. Ma, and J. W. Rogers, Jr., Thin Solid Films, 377-378 (2000) 766-771.

Electrochemistry and Fluid-Solid Interfaces
Room 111 - Session EC-MoA

Electrochemical Control of Surface Structure: Growth and Dissolution

Moderator: C.F. Windisch Jr., Pacific Northwest National Laboratory

2:00pm **EC-MoA1 Local Dynamics of Electrochemical Dissolution and Growth Processes***, **O. Magnussen**,* Universität Ulm, Germany **INVITED**

The active dissolution of a bare metal surface is of central importance for technological processes, such as aqueous corrosion, etching, and electrorefinement. Even on clean, single crystalline electrodes this electrochemical reaction proceeds at a highly non-uniform rate and is strongly localized at a small number of atomic-scale defects ("active sites") on the metal surface, which are commonly identified with kinks in atomic steps on the crystal surface. With the help of in situ scanning tunneling microscopy (STM) a detailed picture of the underlying microscopic mechanisms and dynamics is now emerging. Here, results on the dynamics of dissolution and growth at the solid-liquid interface by novel, STM-based methods with high temporal and spatial resolution are presented. Using high-speed Video-STM with image acquisition rates of up to 25 images per second the underlying atomic-scale processes, such as the nucleation and propagation of kinks along the steps of the crystal surface, can be directly studied, as illustrated for Cu(100) in HCl solution. In particular, it will be shown how the ordered Cl adlayer on this electrode surface determines the structure of active kinks as well as local reaction rates at these sites. Quantitative measurements of the kink propagation rates, i.e., the local dissolution/redeposition rates, reveal high local rates and pronounced local dissolution/redeposition fluctuations at the individual kinks. Even at the onset of Cu dissolution the average kink propagation rates and the average reaction rates at kink sites are in the range of 10@super 3@ and 10@super 5@ atoms s@super -1@, respectively. In addition, these studies give insights into the mechanisms of kink formation during metal dissolution/deposition, which can explain the characteristic surface morphology in this system. Together, these data give a coherent picture of the atomic-scale processes involved in the electrochemical dissolution and growth of Cu(100) in HCl solution.

2:40pm **EC-MoA3 In-situ STM Study of the Formation of Metal Nanostructures of Co on Ag(111)***, D. Marcu, N. Hall, **S. Morin**,* York University, Canada

Recently, there has been a growing interest in the study of the formation of thin metal films and multilayer films of Ni, Co and their alloys due to their interesting magnetic properties. To optimise these materials, we must understand the nucleation and growth processes that are involved in the formation of individual layers. This includes monitoring surface alloying and intermixing processes taking place at the early stages of growth as well as the effect of varying the electrode potential on the formation of these metal films. During this presentation, the electrodeposition of Co and Ni@footnote 1@] on the Ag(111) surface will be compared in terms of their nucleation and growth behaviour in similar electrolytes. Similar to Ni, Co electrodeposition proceeds via preferred nucleation and growth at the substrate step edges at high overpotential. At low overpotential values, the electrodeposition is very slow, with only a few islands nucleating at the step edges. Independently of island nucleation and growth, an adsorbed layer forms on the Ag terraces. This layer appears to be further reduced with time; possible explanations for the origin of this layer will be given. At high overpotential, there is strong evidence of Ag atom mobility, and the resulting substrate changes are only partially removed during Co dissolution. These results will be discussed in the view of possible surface alloying and intermixing between the Co and Ag substrate. These results contrast with previous studies concerning the electrodeposition of Co on Au(111),@footnote 2@ in which no 2D island growth was reported. @FootnoteText@@footnote 1@S. Morin, A. Lachenwitzer, O.M. Magnussen, R.J. Behm, Phys. Rev. Lett., 83 (1999) 5066. @footnote 2@L. Cagnon, A. Gundel, T. Devolder, A. Morrone, C. Chappert, J.E. Schmidt, P. Allongue, Appl. Surf. Sci., 164 (2000) 22.

3:00pm **EC-MoA4 Growth and Dissolution of Surface Structures by Electrochemical Control of Molecular Self-assembly***, Y. He, T. Ye, **E. Borguet**,* University of Pittsburgh

Electrochemical control of molecular self-assembly offers a number of interesting perspectives ranging from molecular electronics to nanostructure formation. Self-assembled alkane monolayers have been observed on both reconstructed and unreconstructed Au(111) surfaces under electrochemical control with STM (scanning tunneling microscopy). The hexadecane molecules appeared as 2.2nm long rods, arranged in parallel rows in high resolution STM images, suggesting an extended molecular conformation. In situ STM enabled the influence of molecular overlayers on surface processes to be monitored in real time following potential driven perturbations. Our results indicate that self-assembled alkane monolayers modify the growth and dissolution of nanoscale islands and can serve as templates for selective deposition of other nanoscale structures.

3:20pm **EC-MoA5 Electrochemical Epitaxial Growth of Palladium Thin Layers on Au(111) and Au(100) Electrodes and Their Electrocatalytic Properties***, **K. Uosaki**, S. Ye, H. Naohara, T. Kondo, K. Tamura,* Hokkaido University, Japan*; M. Takahasi, J. Mizuki,* Japan Atomic Energy Research Institute, Japan

It is well known that the physical and chemical properties of a metal ultrathin layer on a foreign substrate are different from those of the bulk metal.In the present study, the electrochemical epitaxial growth processes of Pd on Au(111) and Au(100) electrodes were investigated by using in situ scanning tunneling microscopy (STM)@footnote 1,2@ and surface X-ray scattering (SXS).@footnote 3@ The effect of the thickness on the electrocatalytic activity for the anodic oxidation of formaldehyde at the Pd thin layers on the Au(111) and Au(100) substrates was also investigated.@footnote 4@ Electrochemical deposition of Pd was carried out in HClO@sub 4@ solution containing PdCl@sub 4@@super 2-@ complex. Electrochemical oxidation of formaldehyde on the deposited Pd layers was studied in HClO@sub 4@ solution containing formaldehyde. In situ STM measurements showed that palladium was grown epitaxially on both the Au(111)@footnote 1@ and Au(100) substrates.@footnote 2@ SXS measurements proved that the lattice parameters of the first Pd layer on

Au(111) and Au(100) substrates were different from those of the bulk Pd crystal but same as those of the gold substrates.@footnote 3@ The electrocatalytic activity for oxidation of formaldehyde depends strongly on the structure and thickness of Pd thin layers. The peak current for formaldehyde oxidation at the Pd/Au(100) surfaces was much higher than that at the Pd/Au(111) surfaces. The peak potentials of anodic peaks corresponding to formaldehyde oxidation were shifted to negative direction as the thickness increased, reflecting the thickness dependent potential shift for oxide formation/reduction on the ultra thin layers of Pd. @FootnoteText@@footnote 1@H. Naohara, S. Ye, K. Uosaki, J. Phys. Chem. B, 102, 4366 (1998). @footnote 2@H. Naohara, S. Ye, K. Uosaki, J. Electroanal. Chem., 473, 2 (1999). @footnote 3@M. Takahashi, Y. Hayashi, J. Mizuki, K. Tamura, T. Kondo, H. Naohara, K. Uosaki, Surf. Sci., Surf. Sci., 461, 213 (2000). @footnote 4@H. Naohara, S. Ye, K. Uosaki, J. Electroanal. Chem., 500, 435 (2000).

3:40pm **EC-MoA6 Electrochemical Deposition of Molybdenum Nanowires for Use as Sensors***, **M.P. Zach**, K. Inazu, J.C. Hemminger, R.M. Penner,* University of California, Irvine

Electrodeposition of molybdenum dioxide (using the step edges of highly oriented pyrolytic graphite as nucleation templates) is used to form precursor nanowires ranging in diameter from 10 nm to one micron with many exceeding one-half millimeter in length. Subsequent treatment with hydrogen gas above 500°C reduces the wires to conductive metallic molybdenum.@footnote 1@ Currently, this is the only method that exists to create millions of ordered nanowires with such high aspect ratios. A polymer film is used to lift the wires off of the conductive substrate thus isolating the wires electronically. The discovery of a method to deposit nanowires is just the beginning. A sensor device can be made by embedding the reduced wires in a polymer, laying a shadow mask over this array, and sputter-coating gold over the unmasked area. In the end, only the nanowires provide a conductive path across the gap left by the mask. The electronic properties of single wires can also be studied using a gold coated probes. The probes can also manipulate individual wires showing flexibility and mechanical properties of the reduced molybdenum and allowing conductivity measurements of single nanowires. Both the sensors and the single wire probe methods for measuring conductivity show decrease of conductivity as a function of time. Understanding the changes in resistance is imperative if these wires or wires made from other materials are to be integrated in functional devices. TEM, EDAX and XPS measurements have allowed characterization of the re-oxidation process in air. Freshly reduced molybdenum wires, upon exposure to oxygen and/or moisture, start to oxidize yielding thinner molybdenum metal wires with a insulating sheath of molybdenum trioxide. This data is important in order to understand the conduction and analyte adsorption properties of wires used in sensor devices. @FootnoteText@ @footnote 1@M.P. Zach and R.M. Penner, Science, December 15, 2000, 290 (5499) 2120.

4:00pm **EC-MoA7 First Observation of Anomalous Scaling in Electrodeposited Films***, **J.J. Mallett**, W. Schwarzacher,* University of Bristol, UK*; N.M. Hasan, S.G. dos Santos,* LSI/EPUSP/Universidade de Sao Paulo, Brazil

The evolution of surface roughness is of importance in most areas of surface physics and can provide useful insights into the nature of surface growth processes. Models of growth often predict surfaces that are statistically self-affine over a range of length scales l << l@sub c@. For such surfaces, the interface width, w, scales as l@super H@, for small l, where l is the length scale over which the roughness is measured. The local surface roughness in the simplest models is found to be independent of the growth time. Many examples of this so called "normal" scaling have been reported to date. Some models also predict the possibility of anomalous scaling, in which the local roughness depends not only on l, but also on the growth time. In this case, known as anomalous scaling, the interface width scales as l@super H@ tsuper@beta@loc, (l << l@sub c@). We report the first electrochemical results consistent with anomalous scaling and investigate the experimental conditions required to produce normal and anomalous scaling surfaces. Galvanostatic electrochemical deposition of copper from additive free acid sulphate solutions was performed onto gold substrates to produce films of various thickness. The interface width, w, was determined, as a function of l, by ex-situ atomic force microscopy. The type of scaling was found to be dependent on the ratio of the deposition current to the diffusion-limited current. At high values of this ratio, anomalous scaling was observed, while normal scaling prevailed at low values. This dependence was found to be independent of the solution concentration and temperature over the ranges measured. These results suggest that bulk diffusion of material to the electrode determines the type of scaling exhibited by the deposited surface.

Magnetic Interfaces and Nanostructures
Room 110 - Session MI+NS-MoA

Nano Magnetics

Moderator: P.N. First, Georgia Institute of Technology

2:00pm **MI+NS-MoA1 Preparation and Magnetic Studies of Mass-Selcted Iron Clusters***, **V. Senz**, R.-P. Methling, A. Kleibert, J. Bansmann, K.E.H. Meiwes-Broer,* Universitaet Rostock, Germany

We have investigated the magnetic properties of mass-selected iron clusters using the magneto-optical Kerr effect (MOKE) in the visible and soft x-ray energy range. Using a continuously working cluster source (Arc Cluster Ion source - ACIS) we codeposited mass-selected iron clusters into a matrix of evaporated silver atoms on a silicon substrate. The source is based on cathodic arc erosion in inert gas environment and supersonic expansion. Its intensity and stability allows an enhanced mass-separation which is achieved by means of an electrostatic quadrupole deflector. Magnetization curves were measured for cluster sizes of 8.1nm and 11.7nm. The hysteresis curves reveal the transition from the ferromagnetic to the superparamagnetic state in dependence on the cluster size and temperature. Recently, element-specific reflectivity measurements have been carried out in the energy range of the Fe 2p core levels using linearly polarized light (X-MOKE). The observed MOKE effect at the 2p levels is much larger than the respective value at the Fe 3d valence band due to the enhanced spin-orbit interaction.

2:20pm **MI+NS-MoA2 Fabrication of Nanomagnet Arrays using Anodic Porous Alumina***, **J.H. Choi**, H.-Y. Kang, W.-G. Park,* Seoul National University, Korea*; Y. Kuk,* Seoul National University, Korea, South Korea

Anodic porous alumina has attracted increasing attention because of its naturally self-ordered porous structure and the capability for the fabrication of dots in nanometer scale. We present two fabrication processes of nanomagent arrays using anodic porous alumina. Electrochemically polished aluminum sheet is anodized in oxalic and sulfuric acid under constant voltage condition and porous alumina is used as a template. Co is electrodeposited in the pore of alumina and the deposition is stopped before Co fills the pore completely. Finally, ion milling is used to remove the upper side of alumina and get smooth surface. In the second process, we use anodic porous alumina as a mold for imprint lithography. Anodic porous alumina is placed on the PMMA/SiO@sub 2@/Co multilayer for the imprint. Hexagonal dot arrays are generated on PMMA and pattern-transferred to lower Co layer using reactive ion etching and ion milling. In both processes, nanomagnet arrays with the size of 40 ~ 100nm are successfully fabricated. The magnetic properties of the particles and their interactions have been investigated by spin polarized scanning tunneling microscopy, magnetic force microscopy and spin polarized scanning electron microscopy.

2:40pm **MI+NS-MoA3 Torques and Tunneling in Nanomagnets***, **D.C. Ralph**, E.B. Myers, M.M. Deshmukh, E. Bonet, F.J. Albert, R.A. Buhrman,* Cornell University **INVITED**

When the size scale of magnetic devices is shrunk to nanometer dimensions, qualitatively new properties can emerge. I will discuss two recent examples. First, I will review investigations of a new mechanism -- spin-transfer -- by which applied currents can be used to manipulate the orientation of ferromagnetic moments. Unlike traditional schemes which utilize a magnetic field to control magnetic reorientation, spin-transfer is based on the exchange interaction. It is a torque that results when a spin-polarized current scatters from a magnetic element, and in the process transfers spin-angular momentum to the magnet. Depending on device geometry and the magnitude of the applied magnetic field, this torque can cause either controlled magnetic reversal or the excitation of high-frequency precession driven by a dc current. Another property that emerges only in devices containing metal grains smaller than about 10 nm in diameter is that the electronic states involved in electron transport can be resolved individually. I will discuss spectroscopic measurements of the electronic states which contribute to electron tunneling in cobalt nanomagnets containing about 1000 atoms, and how these states are influenced by exchange interactions, anisotropy forces, and applied magnetic fields. We find that each electronic state in given magnetic nanoparticle is described by a slightly different anisotropy energy, with fluctuations of order 1 to 3 percent. Individual states are not purely spin-up or spin-down, but have a mixed character. Spin-waves and non-equilibrium excitations play a central role in shaping the tunneling spectrum, even at low energies.

3:20pm **MI+NS-MoA5 Self-assembled Magnetic Dots / Antidots and Dot Chains: Epitaxial Co/Ru(0001)@footnote *@**, ***D. Li***, *C. Yu, J. Pearson, S.D. Bader,* Argonne National Laboratory

We have grown ~ 0-420 nm thick epitaxial Co wedges on flat and grooved Ru(0001) with molecular beam epitaxy at 350 °C to investigate self-assembly in metals and their magnetic properties utilizing ex-situ atomic force microscopy and magnetic force microscope. Three-dimensional islands (dots) or a flat film network with deep holes (antidots) in well-defined truncated pyramidal shapes appear below or above ~ 20 nm, respectively.@footnote 1@ The lateral sizes of these dots/antidots, as well as their spatial distribution on the flat substrates, tend to be uniform at a lengthscale of ~ 10@super 2@ nm in diameter and ~ 10@super 0@ nm in height. This growth mode is mainly driven by strain as a result of an 8% lateral mismatch between the basil plane lattice constants of bulk Co and Ru. On grooved Ru substrates, these self-assembled Co dots align into linear chains along the top and bottom of the grooves. The average dot-to-dot distance within a chain changes from ~ 500 nm to connecting into uniform stripes as a function of coverage. Magnetically, the dots are single domain with in-plane anisotropy. The dot chains have uniaxial anisotropy along the grooves and exhibit dipolar ferromagnetic inter-dot interaction. @FootnoteText@ @footnote *@ Supported by DOE BES-MS #W-31-109-ENG-38. @footnote 1@ Chentao Yu, Dongqi Li, J. Pearson, and S.D. Bader, Appl. Phys. Lett. 78, 1228 (2001).

3:40pm **MI+NS-MoA6 Greatly Enhanced Magnetic Anisotropies in Pure and Bimetallic Co Nanostructures on Pt(111)**, ***T. Cren***, *S. Rusponi, N. Weiss, M. Epple, H. Brune,* Ecole Polytechnique Federale de Lausanne, Switzerland

We report on the enhancement of the magneto-crystalline anisotropy energy K in low dimensional Co islands induced by firm electronic coupling with the underlying Pt(111) substrate. The Co islands were created on Pt(111) using kinetically controlled MBE growth. The correlation between structure and magnetism has been studied by STM and in-situ Surface Magnetic Optical Kerr Effect (SMOKE). We generally observe that the magnetism of the islands is governed by the out-of-plane anisotropy and the M(H)-loops are well described by a two-state Ising model. For pure Co islands, of roughly 1000 atoms size, the shape has only little influence on magnetism (µ=2.2µ@sub B@/atom for ramified and µ=1.9µ@sub B@/atom for compact islands; bulk value 1,7µ@sub B@). From the blocking temperature we deduce an anisotropy energy of K=0.37meV/atom which is greatly enhanced as compared to the Co bulk value of K=0.7µmeV/atom. For double layers islands K is reduced by a factor of two (K=0.16meV/atom) which clearly demonstrates the role of the Co/Pt interface. Finally, we show that the anisotropy can further be enhanced by decoration with Pd or Pt and by bimetallic alloy islands.

4:00pm **MI+NS-MoA7 Invited Paper**, ***A.D. Kent***, New York University **INVITED**

5:00pm **MI+NS-MoA10 Collective Behavior in Patterned Nanomagnetic Dot Array - A Promising Route to Magnetic Data Processing at Room Temperature**, ***A.J. Bennett***, *J.M. Xu,* Brown University

It is well known that nanomagnetics could greatly improve data storage. In this work, through theory and experiment, we show that nanomagnetic patterned arrays are equally promising for data processing. Such arrays offer many potential advantages over CMOS circuits of the same scale: power dissipation drops through magnetostatic signal transport replacing resistive and radiative transmission lines; noise resistance is increased by low environmental coupling; interconnection problems are mitigated by signal transfer via "wireless" interactions. Magnetic interaction simulations using typical parameters suggest that room temperature operation is feasible. Experimental evidence and first-principles analysis will be presented to support this finding. We demonstrate specific nanomagnetic arrays which exhibit basic logic functions. We also show that the implementation of these arrays is within the reach of a hybrid strategy of e-beam lithography and a new non-lithographic nanofabrication technique our lab has developed (to be described in a separate report). Modeling collective behavior and designing nanomagnetic array logic represent new challenges which are met by a full-interaction-matrix Monte Carlo technique we developed. This approach enables simulation of nanodisk lattices as well as engineered branched arrays and gates for general logic. Unlike a nearest-neighbor model, our approach includes all interactions; thus, we may predict and compensate for problems arising from long-range interactions which arise in large circuits. In conclusion, magnetic nanostructures and nano-array gates show significant promise for nanoscale, room-temperature information processing.

Manufacturing Science and Technology
Room 131 - Session MS-MoA

Manufacturing Technologies for the Information Industry

Moderator: M. Surendra, IBM T.J. Watson Research Center

2:00pm **MS-MoA1 Silicon on Insulator for 100 nm Generation System on Chip**, ***G. Shahidi***, IBM Microelectronics Division **INVITED**

SOI CMOS has become a mainstream CMOS technology. In this paper, we will first give a brief overview of the key attributes and challenges of SOI CMOS. As we scale CMOS into 100 nm and beyond, SOI opens novel opportunities, where bulk CMOS is approaching its limits. We will review the extendibility of benefits of SOI (performance gain and floating body effects at 100 nm and beyond). SOI opens some very exciting opportunities in RF CMOS, low power, and other elements needed for system on chip. SOI CMOS is the technology to use when high performance, low power, and capability to easily integrate other needed elements for SOC, at CMOS generations beyond 100 nm.

2:40pm **MS-MoA3 Integrated Circuit Challenges for sub-100nm Generations**, ***M. Bohr***, Intel Corp. **INVITED**

This talk will cover the challenges faced as transistors and interconnects are scaled to sub-100nm dimensions and review some of the device and material options being investigated to meet these challenges.

3:20pm **MS-MoA5 The Future for Storage Technology and Manufacturing**, ***M. Re***, Read Rite Corp. **INVITED**

4:00pm **MS-MoA7 An Overview of Manufacturing Processes of Some Passive and Active Components for Fiberoptic Communication Networks**, ***N.A. O'Brien***, *S.P. Sapers,* JDS Uniphase Corporation **INVITED**

The wide proliferation of the Internet in the mid 1990s has led to an exponential growth in bandwidth demand. The fiberoptic communications industry was faced with the option of installing more fiber and increasing the bit rate from 10 Gbit/sec in the existing communication systems by, time division multiplexing (TDM). In TDM systems, multiple signals of one wavelength are transmitted through a single fiber but are distinguished from each other by specific time intervals. That option was not economically viable. Wavelength division multiplexing (WDM) emerged as the new technology that increases the capacity of existing fiber by sending multiple (multiplexing) wavelengths down one fiber. The total bandwidth per fiber is the sum of the bit rate of each wavelength. Systems have been built with up to 128 wavelengths per fiber. There are several competing technologies that are employed for multiplexing and demultiplexing such as thin film interference filters, fiber Bragg gratings, and arrayed waveguide gratings. While WDM has kept up with the increase in bandwidth demand, fiberoptic communication systems still rely on optical-to-electrical conversion for switching purposes. This leads to inflexibility of the systems, increased maintenance, and high costs. There exists a great need to have an all-optical network. Recent developments in micro-electro mechanical systems (MEMS) provide a great promise towards making that a reality. MEMS are nanodevices. They are often likened to integrated circuits (ICs) due to similarities in size and manufacturing methods, except ICs route electrons and MEMS can route photons. WDM filter technology has matured and has become yesterdayâ€™s news, while MEMS applications remain in development stages but near commercialization. This presentation is structured to talk about WDM filter technologies and MEMS in the context of passive and active devices respectively, with emphasis on the manufacturing processes.

4:40pm **MS-MoA9 Scientific Challenges in Harnessing Molecules for Electronic Devices**, ***D.L. Allara***, Pennsylvania State University **INVITED**

Recent work has shown that molecules are capable of functioning as electronic components such as resistors, diodes and switches. These fundamental properties, in principle, can lead to new generations of devices and computing machines. However, many fundamental challenges lie ahead as the implementation of these technologies begins. These challenges include issues of chemical assembly, lithographic scales and electrical contacts. These and other aspects will be presented and discussed from a broad point of view with an emphasis on the underpinning science that is needed to help enable process development.

Processing at the Nanoscale
Room 133 - Session PN-MoA

Nanostructures from 0 to 3 Dimensions

Moderator: H.G. Craighead, Cornell University

2:00pm **PN-MoA1 Inorganic Nanorods: Synthesis, Alignment, and Properties***, **A.P. Alivisatos,*** University of California, Berkeley **INVITED**

Inorganic nanocrystals with well defined shapes are important for understanding basic size-dependent scaling laws, and may be useful in a wide range of applications. Methods for controlling the shapes of inorganic nanocrystals are evolving rapidly. This talk will focus on a strategy that involves pyrolysis of organometallic precursors in mixtures of hot organic surfactants. The surfactant mixtures can be used to control the growth rates of different facets of the nanocrystals, allowing for wide tunability of shape. This will be illustrated with CdSe and Co nanocrystals. Both of these materials show pronounced variation of fundamental properties with aspect ratio. The nanorods can be aligned in a variety of ways. For instance, monolayers of surfacatant coated rod-like nanocrystals of these materials display a very rich phase diagram, analogous to the phases of liquid crystals. Block copolymers can be used to orient the rods. Finally, very special inorganic structures, tetrapods consisting of four rods at the tetrahedral angle, will always spontaneously align perpendicular to a surface. The possible application of these aligned nanorods in biological detection, photovoltaics, and light emitting diodes will be described briefly.

2:40pm **PN-MoA3 Interfacial Controlled, Self-assembled Copper-Oxide Nano-dots and Rings on SrTiO@sub3@(001)***, **Y. Liang**, D. McCready, S. Lea,* Pacific Northwest National Laboratory

Since oxides exhibit a much wider range of novel electronic, optical, magnetic, and dielectric properties than semiconductors and metals, oxide nano-structures have the potential to provide systems with much higher functionality and richer behaviors. We have successfully synthesized copper oxide nano-dots and rings on SrTiO@sub3@ substrates using oxygen-plasma assisted molecular beam epitaxy. The morphological, structural, chemical, and electronic properties were examined by XPS, AFM, scanning Auger microscopy, and high-resolution XRD. Four types of nanostructures were found under different synthesis conditions: truncated dots, square pyramids, multifaceted domes, and corral-like rings. XPS measurements on band offsets show that Cu@sub2@O/SrTiO@sub3@ exhibits a type-II heterojunction with both the valance and conduction bands of Cu@sub2@O higher than that of SrTiO@sub3@, i.e quantum dot for electrons but anti-quantum dot for holes. Consequently the photo-excited electrons and holes are spatially separated with holes being confined to Cu@sub2@O quantum dots and electrons confined to SrTiO@sub3@, a property important for photocatalysis and other applications. We are currently using the surface-potential AFM and magnetic-force microscopy to elucidate the nano-scale spatial charge separation from the nanodots and the induced magnetic property from the nano-rings. @FootnoteText@ Pacific Northwest Laboratory is a multiprogram national laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

3:00pm **PN-MoA4 Charge Mediated Selective Reaction and Assembly of Functional Nanostructures***, **T. Alvarez**, S.V. Kalinin, D.A. Bonnell,* University of Pennsylvania

A primary challenge in fabricating functional devices with nanometer scale components is to position and connect a number of dissimilar electroactive device elements in a predefined scheme. We will demonstrate the use of local electric fields to constrain selective chemical reactions that produce and position metallic nano contacts and metallic wires. The local electric fields are induced by atomic polarization in a semiconducting ferroelectric substrate. Nanometer scale (30-80 nm) metal nanocontacts are deposited by photoreduction and the size dependence of interface contact potential quantified. Subsequent reactions similar to conventional self-assembly allow functional elements such as organic molecules that act as diodes or NDR devices to develop into complex structures. Atomic polarization, charge compensation in the substrate, and local properties of nanocontacts are characterized with variants of scanning probe microscopy. The approach will be demonstrated with Ag nanocontacts on BaTiO3 substrates. The generalization of the approach to broader materials sets and to 3-D structures will be discussed.

4:00pm **PN-MoA7 Size Selective Electrochemical Growth of Molybdenum Disulfide Nanowires and Nanoparticles***, **K.H. Ng**, K. Inazu, R.M. Penner, J.C. Hemminger,* University of California, Irvine

MoS@sub 2@ nanoparticles and nanowires having mean diameters ranging from 2 to 200 nm were synthesized on the basal plane and step edges of highly oriented pyrolytic graphic surface using an electrochemical/chemical (E/C) method. This method involves the following steps: (1) electrochemical deposition of molybdenum dioxide precursor nanostructures consisting of nanowires or nanoparticles onto an electrode surface, (2) displacement of oxygen in MoO@sub 2@ with sulfide by heating the sample at 500°C in H@sub 2@S. Each metal oxide nanostructure was converted into a semiconductor nanoparticle of the same shape and size as the original MoO@sub 2@ precursor nanostructure. Selected-area electron diffraction (SAED), energy dispersive X-ray analysis (EDX) and X-ray photoelectron spectroscopy (XPS) confirm the formation of MoS@sub 2@ nanostructure. For MoS@sub 2@ nanostructure having a critical dimension larger than 20 nm, photoluminescence spectroscopic analysis showed a strong, room temperature emission peak around 2 eV which is consistent with the direct bandgap of this material. As the critical dimension was reduced from 20 to 2 nm, the energy of this emission shifted to higher energies qualitatively as predicted by the effective mass, strong confinement model.

4:20pm **PN-MoA8 Generation of Self Organized Nanometer Structures on Surfaces of Ionic Solids Generated by Electron and Laser Beam Irradiation - The Role of Water***, **K. Nwe**, S.C. Langford, J.T. Dickinson,* Washington State University

Radiation effects on hydrated single crystals are poorly understood. We find that dense ordered arrays of nanoscale conical structures, with aspect ratios greater than 200, are produced when single crystal brushite (CaHPO4.2H2O) is exposed to energetic electrons (2 keV). All cones are pointed directly towards the incident electron beam. Other three dimensional nanostructures are generated by exposing brushite to excimer laser irradiation. We show that the mechanism involves: (a) photo/electron stimulated decomposition of the matrix, and (b) thermally stimulated migration of water (in this case, crystalline) and ionic material. We have isolated these factors and present plausible mechanisms for structure formation where water plays a dominant role. In addition, we have recently exposed non-hydrated ionic crystals to radiation in the presence of background water at partial pressures of 10-7 Torr, which yields exceedingly fine structures (sub-10 nm). These materials show very interesting optical and luminescence properties which we will present. Finally, we show that in the presence of water vapor, the rates of both laser and electron beam induced decomposition/desorption increase by as much as an order of magnitude. We present evidence that this is a highly localized, defect mediated mechanism.

5:00pm **PN-MoA10 Optical Behavior In Semiconductor-Transparent Conducting Oxide Nanocomposite Thin Films Fabricated by RF Magnetron Sputtering***, **T.J. Bukowski**, K. Simmons-Potter,* Sandia National Laboratories*; P. Lucas, J.H. Simmons,* University of Arizona

Semiconductor nanocrystals were fabricated within a transparent conducting oxide matrix using a dual gun rf magnetron sputtering system. The resulting nanocomposite film is composed of a multilayer structure with controllably thin semiconductor layers forming isolated clusters. Through manipulation of the deposition conditions and subsequent anneals, the size of the nanocrystals can be tailored. This work examines the optical behavior of germanium quantum dots surrounded by indium tin oxide (ITO). ITO has transmittance as high as 90% and resistivities in the range of 7x10@super -5@-5x10@super -4@ @OMEGA@cm. The presence of a transparent conducting oxide matrix surrounding the semiconductor nanoclusters can lead to interesting optical and electronic properties, having exciting photoconductive and photovoltaic applications. Raman and absorption spectroscopies are used to study the development and structure of the multilayer films and to observe changes due to the quantum confinement effect. Photoconductivity is also reported in order to gain insight into the electronic properties of the nanocomposite.

Plasma Science
Room 103 - Session PS1-MoA
Plasma-Surface Interactions I

Moderator: S. Han, University of New Mexico

2:20pm **PS1-MoA2 In-vacuo Electron-Spin-Resonce Study on Fluorocarbon Films for SiO@sub 2@ Plasma Etching***, **K. Ishikawa**, S. Hayashi, M. Okigawa, S. Kobayashi, M. Sekine, M. Nakamura,* Association of Super-Advanced Electronics Technologies (ASET), Japan*; S. Yamasaki, T. Yasuda, J. Isoya,* Joint Research Center of Atom Technology (JRCAT), Japan

An in-vacuo electron spin resonance (ESR) setup opens the new experimental approach to the understanding the microscopic chemical reactions in etching process. Creation of dangling bonds (DB), namely, bond breaking, is indeed a key process for etching mechanism and created DB are playing an important role for surface reactions. The in-vacuo ESR technique is applied to the studies of surface, on which fluorinated carbon (a-C:F) film exists, during fluorocarbon gas etching processes of an amorphous SiO@sub 2@ film. In this work, we prepared a capacitively-driven reactor which is connected with an ESR system through a wafer transfer system. An a-C:F film was deposited on a crystalline Si substrate with 20 nm thickness which is estimated using cross-sectional transmission electron microscopy. The carbon DB signal in a-C:F film was observed after transferring to the ESR cavity under vacuum ambient. This signal are stable as long as the sample is kept in vacuum, however, once the sample was exposed to air, the signal intensity drastically decreased. The decrease of ESR intensity by air exposure points out that the oxygen molecules penetrate deeply into the a-C:F film, and terminate spin centers in the film. This technique can be applied to the reaction of a-C:F films with oxygen atoms with a bottom layer of SiO@sub 2@ films for the case of SiO@sub 2@ etching processes, the selectice etching mechanisms. @FootnoteText@ This work was supported by NEDO.

2:40pm **PS1-MoA3 The Deposition on and Etching of Si(100) by Large, Hyperthermal Fluorocarbon Ions***, L. Hanley, **E.R. Fuoco**, M.B.J. Wijesundara,* University of Illinois at Chicago

Fluorocarbon plasmas are commonly used to etch features into Si wafers for the production of microelectronic circuits. It has been postulated that large fluorocarbon ions participate in both etching the Si and deposition of a fluorocarbon thin film on Si that hinders etching.@footnote 1@ We study the ability of mass-selected beams of large, hyperthermal fluorocarbon ions to deposit films on and etch Si(100). 25 to 200 eV C@sub2@F@sub4@@super+@ and C@sub3@F@sub5@@super+@ ions are deposited H-Si(100) and x-ray photoelectron spectroscopy is used to analyze the resultant fluorocarbon films. The disappearance of the Si(2p) peak in the survey spectra indicates that lower energy C@sub3@F@sub5@@super+@ ions create a continuous, relatively thick film as ion fluence is increased. On the contrary, higher energy C@sub3@F@sub5@@super+@ ions create a film that is self-limiting. As the ion fluence is increased, the film thickness stays constant. The C(1s) core level spectra contain the same fluorinated carbon components at all energies. A comparison of two different ions, C@sub2@F@sub4@@super+@ versus C@sub3@F@sub5@@super+@, show close similarities in the C(1s) core level spectra leading to the conclusion that the identity of the ion does not significantly change the chemical composition of the deposition. Atomic force microscopy is also employed to view the morphology change of the different energy deposits. These results are discussed in terms of the role of large fluorocarbon ions in the plasma etching of Si(100). @footnote 1@M.B.J. Wijesundara, Y. Ji, B. Ni, S.B. Sinnott, L. Hanley, J. Appl. Phys. 88 (2000) 5004 and references therein.

3:00pm **PS1-MoA4 Gas-Phase Chemistry of SiN PECVD Process at Ambient Pressure***, **G.R. Nowling**, S.E. Babayan, X. Yang, M. Moravej, R.F. Hicks,* University of California, Los Angeles

The plasma-enhanced chemical vapor deposition (PECVD) of silicon nitride films has been examined in an atmospheric-pressure, helium-nitrogen discharge. The concentrations of the active nitrogen species in the afterglow have been determined by optical emission and absorption spectroscopy. For operation with 752 Torr N2 and 8 Torr He, at 32.9 (W/cm^3) RF power, and a 40.4 L/min flow rate, the plasma produced 4.8x10^15 cm^-3 of N, 2.1x10^13 cm^-3 of N2(A), 1.2x10^12 cm^-3 of N2(B), and 3.2x10^9 cm^-3 of N2(C). As the gas enters the afterglow, the concentrations of the active molecular nitrogen species drop by at least two orders of magnitude. However, the ground-state atomic nitrogen atoms remain at a high concentration due to their slow rate of recombination by three-body collision. Spectroscopic measurements made of the gas and surface during PECVD indicate that the dominant reaction pathway is heterogeneous, i.e., occurs on the surface of the silicon nitride film. A numerical simulation has been developed which models the coupled fluid dynamics, gas-phase kinetics and surface reaction kinetics. These results together with the experimental measurements will be presented at the meeting.

3:20pm **PS1-MoA5 Study of Surface Reaction of SiO@sub 2@ Etching by Plasma Beam Irradiation***, **K. Kurihara**, Y. Yamaoka, M. Sekine, M. Nakamura,* Association of Super-Advanced Electronics Technologies (ASET), Japan

Fluorocarbon gases are widely used for Si/SiO@sub 2@/SiN etching to achieve high etching performance. The SiO@sub 2@ etching mechanism has been studied for the last three decades by using etching reactors and beam apparatuses. Multi-beam (ions and/or radicals) experiments are useful for understanding the surface reaction by simplifying beam-surface interaction. However, the plasma surface reaction in the etching reactor is very complicated because of many kinds of ions and radicals especially for fluorocarbon gas case. We have constructed a plasma-beam irradiation apparatus to examine the plasma-surface reactions under a real etching environment. Our plasma source can control plasma parameters, such as ion energy, residence time of introduced gases, radical/ion composition, and the ratio of a neutral flux to an ion flux. Desorbed products from the SiO@sub 2@ substrate were measured by a quadrupole mass spectrometer (QMS) during CF@sub 4@/Ar gas mixture plasma beam irradiation. The desorbed products from SiO@sub 2@ are assumed to be SiFx, COFx, (x=1-3), CO, CO@sub 2@ etc. However, SiFx and COFx can not be detected separately by QMS because they have the same atomic mass. Therefore, CF@sub 4@ gas which consists of isotope C@super 13@ was used as an etching gas in order to discriminate between SiFx and COFx. It was found that major Si containing desorbed products were SiF@sub 2@ and SiF@sub 4@. Their composition, furthermore, did not strongly depend on the ion energy in the range from 300eV to 800eV. After the plasma-beam irradiation, the surface of the substrate was examined by an in-situ XPS analysis. The fluoro-carbon (CF) layers on the SiO@sub 2@ were very thin, about 0.1-0.2 nm. The thicknesses of CF layer and their properties (F/C ratio and binding states) were found to be not dependent on the ion energy. This work was funded by NEDO.

3:40pm **PS1-MoA6 Plasma Polymer Deposition and Permeation into Porous Substrates***, S. Datta, J. Zhao, J. McDaniel,* Procter & Gamble*; S. Mukhopadhyay, **P. Joshi**,* Wright State University

Plasma polymerization for surface modification is gaining increased attention for industrial applications. Commercial efforts are focused, for example, on creating barrier coatings on food packaging and film-type substrates. However, another class of materials that can benefit from surface modification processes is porous substrates such as non-woven materials and woven fabrics. These materials are important for both consumer and industrial applications. Plasma polymerization is viewed as a surface modification process, that generally alters the top one micron layer of material, with no impact on bulk properties. However, for porous substrates such as fabrics and non-wovens, plasma polymerization of external as well as internal surfaces within the bulk material are important. To date, there have been few studies focused on the permeation of plasma polymerization through porous materials. This study was aimed at understanding the impact of various processing as well as substrate parameters on the permeation of plasma polymerization into porous materials. Cellulose-based filter paper was used to investigate the deposition profile and penetration of plasma treatment through porous materials. Several five or ten layer stacks of filter paper, each having different particle detention rating (different pore size) were used as model porous substrates. Plasma polymerized perfluoromethylcyclohexane (PFMCH) was deposited on these stacks and subsequent analysis of each layer in the stack was performed using X-ray photoelectron spectroscopy (XPS), contact angle measurements and water absorption rates. Correlation between these quantities will be discussed in light of the microstructure of these papers as seen by optical and electron microscopy. The dependence of plasma penetration depth upon (a) plasma parameters, (b) filter paper pore size and (c) duration of plasma treatment will be presented. @FootnoteText@ @Footnote *@J. Zhao - Current address : March Instruments, Concord, CA.

4:00pm **PS1-MoA7 Mechanisms for Surface Interactions of NH@sub x@ Radicals During NH@sub 3@ Plasma Processing of Metal and Polymer Substrates***, C.I. Butoi,* Primax, Inc.*; M.L. Steen,* ***E.R. Fisher,*** Colorado State University

The chemistry occurring at surfaces of substrates during plasma processing of polymers and metal surfaces is complex. For example, ammonia plasmas have been used to increase adhesion properties between metals and other materials and to create hydrophilic surfaces. We have examined interactions of NH and NH@sub 2@ radicals with different substrate materials during NH@sub 3@ plasma processing. NH@sub 2@ scatter coefficients, S, were obtained as a function of applied rf power (P) for polymer, silicon, and metal substrates. In most cases, S @>=@ 1, indicating NH@sub 2@ surface generation occurs at the plasma-substrate interface. Energy transfer between NH@sub 2@ and substrates was evaluated via translational temperatures for scattered NH@sub 2@ molecules, @THETA@@sub Tsc@. Translational temperatures for NH@sub 2@ molecules scattered from Pt, Cu, and Si substrates show little dependence on P, while NH@sub 2@ scattered from polymers have linear increases in @THETA@@sub Tsc@, changing by as much as ~120 K for P = 50-150 W. S and @THETA@@sub Tsc@ values measured using an ion-free molecular beam indicate ions increase both kinetic energy and amount of scattered NH@sub 2@. Examination of possible reaction pathways suggests that H atom abstraction by NH radicals may contribute to the observed surface generation of NH@sub 2@. Surface reactivity measurements for NH radicals on polymer surfaces show S < 1, consistent with this mechanism. The effects of P, substrate material and the presence of ions on NH surface interactions are presented, providing additional insight into the underlying mechanisms for NH@sub 3@ plasma processing of both polymer and metal surfaces. These surface interaction data will be presented along with mass spectral data and surface analysis, thereby providing a fairly comprehensive view of the ammonia plasma processing system.

4:20pm **PS1-MoA8 Plasma Chemistry, Plasma-surface Interaction, and Surface Reactions during a-Si:H and a-SiN@sub x@:H Deposition***,* ***W.M.M. Kessels,*** Eindhoven University of Technology, The Netherlands, Netherlands*; E.R. Fisher,* Colorado State University*; E.S. Aydil,* University of California, Santa Barbara*; M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands **INVITED**

Insight into the growth mechanism of plasma deposited materials is essential for full optimization and complete exploitation of the opportunities of plasma assisted deposition. Unraveling the growth mechanism requires investigation of the three different aspects of the deposition process: the plasma chemistry, the plasma-surface interaction, and the surface reactions converting surface species into bulk film. In this presentation, these three aspects will be considered and illustrated by studies on the radical dominated deposition process of hydrogenated amorphous silicon (a-Si:H) and silicon nitride (a-SiN@sub x@:H). From mass spectrometry and spectroscopic studies, the plasma species and their production and loss mechanism in plasmas of SiH@sub 4@ and mixtures with N@sub 2@ and NH@sub 3@ will be considered. From the density of the different species in the plasma their contribution to film growth has been determined. The surface reactivity and the reactions of the SiH@sub x@ and NH@sub x@ radicals on the surface will be treated as investigated by the laser-induced fluorescence (LIF) based "imaging of radicals interacting with surfaces" (IRIS) technique and the newly developed time-resolved cavity ring down spectroscopy (@tau@-CRDS). The nature of the surface during deposition and its connection with the surface reactions will be discussed using in situ attenuated total reflection infrared (ATR-FTIR) measurements of the chemisorbed SiH@sub x@ and NH@sub x@ surface hydrides. From the combination of results and the relations with the material properties, the kinetic growth models of the materials will be reviewed and further refined and extended.

5:00pm **PS1-MoA10 Arc Generation from Sputtering Plasma-Dielectric Inclusion Interactions***,* ***C.E. Wickersham****, J.E. Poole, A. Leybovich, J. Fan, L. Zhu,* Tosoh SMD, Inc.

Arcing during sputtering and etching is a significant cause of particle defect generation during device fabrication. The size of the dielectric inclusion plays a major role in determining if arcing occurs and particle defects are generated. We studied the effect of inclusion size, material type and plasma conditions on the propensity for arcing during sputtering of aluminum targets. We have found that there is a critical inclusion size required for arcing to occur. The critical size for Al@sub 2@O@sub 3@ inclusions in an aluminum target under typical magnetron sputtering conditions is 440 ± 160 µm. Inclusions with sizes above this critical value readily induce arcing and macroparticle ejection during sputtering. Inclusions below this critical size do not cause arcing or macroparticle ejection. High-speed videos were used to study the arc initiation and behavior. The effect of inclusion aspect ratio and inclusion material type such as SiO@sub 2@, TiO@sub 2@, Al@sub 2@O@sub 3@, CaO, Ta@sub 2@O@sub 5@, AlN and BN on the arcing behavior of aluminum targets were also studied. When the inclusion size exceeds the critical value the sheath over the inclusion is deformed by the charge accumulating on the dielectric inclusion and the plasma positive column distorts toward the target leading to a bipolar arc. Inclusions below the critical size do not distort the sheath to an extent great enough to permit bipolar arc formation. Our proposed model predicts that the critical inclusion size depends upon the sheath thickness, which ranged between 300 and 600 µm for the experimental conditions used in this study.

Plasma Science
Room 104 - Session PS2-MoA
Plasma Modification of Organics

Moderator: D.B. Graves, University of California at Berkeley

2:00pm **PS2-MoA1 Treatment of Bone Tissue using an Inductively Coupled Plasma***,* ***C.Y.M. Maurice****, J.H.R. Feijen, E. Stoffels, G.M.W. Kroesen,* Eindhoven University of Technology, The Netherlands

Nowadays, the frontiers between physics, chemistry and biology are disappearing: polymer films are deposited via plasma processes, and numerous applications for medical purposes are emerging every day. However, the actual consequences of plasma interactions with organic matter have not yet been resolved. One of the interesting plasma applications is the possibility of refined modification of bone tissue. In this work we investigate the impact of positive ions formed in a low-pressure plasma on the bone surface. The sample is subjected to controlled ion bombardment and the post treatment response is investigated using microscopy. For plasma treatment we employ a low pressure Inductively Coupled Plasma (ICP) source. This type of reactor is capable of independently control the energy and the density of the positive ions impinging on the surface. At present, it is used for selective etching of inorganic samples. To monitor the ion energy, an energy resolved mass spectrometer is placed at the plane of the sample on the bombarded electrode and records the Ion Energy Distribution Functions. A Langmuir probe gives densities and potential measurements in the bulk plasma and the DSLIF (Doppler Shifted Laser Induced Fluorescence) technique gives access to IVDFâ€™s (Ion Velocity Distribution Functions) of the plasma ions. We characterise the plasma produced ions while processing the bone samples. This kind of treatment can have a large impact on the structure of the bone surface, such as reducing micro fractures, or selectively removing cancer cells. Understanding plasma-surface interactions under vacuum conditions may be useful in the future for the design of an atmospheric plasma source for bone treatment.

2:20pm **PS2-MoA2 Nitrogen Uptake Kinetics of Poly(ethylene-2,6-naphthtalate) Webs in Low-Radiofrequency Nitrogen Discharges***,* ***J.M. Grace****, H.K. Zhuang, L.J. Gerenser, D.R. Freeman,* Eastman Kodak Company

Low-radiofrequency capacitively coupled nitrogen discharges are surprisingly effective at modifying the surface chemistry of polymeric materials. Such discharges are likely to have a variety of energetic species. Furthermore, the variety of interactions that such species may have with surface atoms in the repeat unit of a polymer such as poly(ethylene-2,6-naphthalate) (PEN) is considerable. Hence, it is difficult to determine the dominant surface reactions responsible for the chemical modification. Nonetheless, it is helpful to examine the nitrogen uptake kinetics and compare them with inferred species fluxes to gain insights into the surface modification process. Using optical emission spectroscopy (OES) and ion flux probe (IFP) techniques, fluxes of atomic nitrogen and ions were measured in a relative sense over a range of discharge conditions. X-ray photoelectron spectroscopy was used to measure the nitrogen content of the PEN surface as a function of exposure time at given discharge conditions. The OES and IFP data suggest that applied power primarily controls the flux of ions to the substrate, while pressure primarily controls the flux of atomic neutral nitrogen. Using a surface sites model to interpret the nitrogen uptake data it is found that ion flux, neutral atomic nitrogen flux, and their interaction contribute to the nitrogen uptake rate, with the interaction term being quite significant. This apparent ion-neutral synergy suggests a two-step nitrogen incorporation process consisting of formation of a surface radical by ion bombardment (or by some other species whose flux scales with the ion flux), followed by reaction with atomic neutral nitrogen. In addition, direct reaction of atomic ions or atomic neutrals may contribute to the nitrogen uptake rate. Using the parameters obtained from analysis of the linear uptake regime, analysis of the surface saturation regime suggests that sputtering and recombination both contribute to loss of surface nitrogen.

2:40pm **PS2-MoA3 Control of Spatial Distribution of Adsorbed Proteins Using Plasma Surfaces*, N.A. Bullett,*** University of Sheffield, U.K.*; R.D. Short,* University of Sheffield, U.K., UK*; C.W.I. Douglas,* University of Sheffield, U.K.

The adsorption of proteins occurs whenever a material contacts with biological media. In cell culture, proteins rapidly adsorb to the plastic from serum and the adsorbed protein layer subsequently influences cell adhesion, proliferation and differentiation. The ability to control and direct specific protein adsorption and conformation would enable culture surfaces to actively influence the behaviour of cells. This work aims to show that we can exert a degree over control of the adsorption and conformation of proteins from both single solution and serum. The ability to control the spatial distribution of adsorbed proteins will also be demonstrated. Plasma-co-polymerisation of acrylic acid with 1,7-octadiene was used to create a range of carboxylic acid functionalised surfaces. Protein adsorption to these surfaces was measured using an antibody recognition technique (ELISA) and radio-labelling, FITC-labelling and XPS analysis of adsorbed proteins. For single protein solutions and serum, radio-labelling, FITC-labelling and XPS showed a decrease in the amount of adsorbed protein binding with surface acid content. ELISA results would appear to show the opposite, more protein binding to the acid functionalised surfaces. This apparent contradiction in data may be explained by a change in the nature of the adsorbed proteins. Chemical micropatterns were created by the plasma polymerisation of either acrylic acid or allyl amine onto 1,7-octadiene through TEM grid masks. Imaging ToF-SIMS and XPS was used to verify the chemical differentiation in the surface. The micropatterned surface was shown to influence the adsorption and spatial distribution of FITC-labelled adsorbed proteins.

3:00pm **PS2-MoA4 Characterization of Pulsed Plasma Chemistry for the Deposition of Polyethylene Glycol-like Polymer Thin Films*, D.C. Guerin,*** Naval Research Laboratory, National Research Council*; D.D. Hinshelwood, V.A. Shamamian,* Naval Research Laboratory

We have deposited organic thin films with pulsed RF inductively coupled plasmas. We used two organic precursors, isopropyl alcohol and 1,4 dioxane, in argon. We characterized the plasmas with Langmuir probe measurements. Using in situ mass spectrometry, we identified the primary ionized species that diffuse to the surface. These species are different for the two precursors. We propose mechanisms for the creation of these species, which are primarily electron-impact dissociation ionization and ion-molecule reactions. Tuning the plasma parameters varied the mass distributions of the ionic flux to the surface. For example, at low pressure, the species due to electron-impact were predominant. We also used the mass spectrometer to measure the flux of neutral species to the surface. We determined that varying the plasma conditions has a large effect on the relative importance of ions and neutrals in the deposition process. At certain pressures and RF power levels, the flux of reactive neutrals is minor compared to the ion flux, which dominates the deposition process. X-ray photoelectron spectroscopy was performed on the samples. For isopropyl alcohol, a simple relation was discovered between the ion mass distributions and the chemical bonding character of the deposited film.

Semiconductors

Room 122 - Session SC+SS-MoA

Semiconductor Surfaces

Moderator: D.Y. Petrovykh, Naval Research Laboratory

2:20pm **SC+SS-MoA2 Indium-Induced Charge Redistribution and Surface Electronic Structure of the Si(111)-(7x7) Surface*, M. Yoon,*** *R.F. Willis,* The Pennsylvania State University

The adsorption mechanism and the origin of the In-induced surface electronic states of the Si(111)-(7x7) surface have been studied using bias-dependent scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS). At very low In coverages, bias-dependent STM images show that some of adatoms have either slightly higher or lower apparent height in the filled-state image, while the empty-state images are completely identical to those of the clean Si(111)-(7x7). These peculiar features are interpreted as being caused by two adsorption mechanisms: charge redistribution due to the adsorption of In atoms on Si dangling bond and the substitution of In for Si atoms in the 7x7 adatom positions, opening the bandgap by removing intrinsic metallic surface states caused by Si adatom dangling bond. As the coverage increases, a self-assembly of a superlattice of two-dimensional non-metallic In nanodots on the Si(111)-(7x7) surface begin to develop on both halves of the 7x7 unit cell which indicates a metal-insulator transition occurring on the surface. This confirms that the origin of the metallicity of the Si(111)-(7x7) surface is the delicate charge transfer between adatom and restatom Si dangling bonds in the center of the 7x7 unit cell.

2:40pm **SC+SS-MoA3 Study of GaAs(100) Surface Cleaning Using Synchrotron Radiation Photoemission Spectroscopy*, Z. Liu,*** *Y Sun, F. Machuca,* Stanford University*; W.E. Spicer, P. Pianetta,* Stanford Synchrotron Radiation Lab*; R.F.W. Pease,* Stanford University

Atomic surface cleanliness is required for novel NEA electron emission devices fabricated from GaAs and is also very important for GaAs MBE growth. Chemical cleaning of the GaAs (100) surface has been studied with high-resolution photoemission spectroscopy using synchrotron radiation (in the range of 55 eV to 750 eV) at the Stanford Synchrotron Radiation Laboratory. The high surface sensitivity of the technique has allowed us to identify the chemical state of the surface species after both the chemical cleaning and final vacuum processing steps. In order to eliminate contamination from the surroundings, all chemical cleaning steps were performed in an Ar or N@sub 2@ purged glove box attached to the load-lock allowing samples to be transferred into the system without being exposed to air. Samples were etched in H@sub 2@SO@sub 4@:H@sub 2@O@sub 2@:H@sub 2@O solution and then heat cleaned at 500°C (both diluted and concentrated solutions were studied). After chemical etching in the dilute (4:1:100) solution, elemental As (>1ML), As sub oxide (~0.1ML), Ga sub oxide and C (0.5~1ML) are found on the surface. Subsequent annealing at 500°C in UHV produces a stoichiometric, oxide free surface as determined by valence band and core level photoemission. In addition, C has been reduced to less than 10% of its initial level. We believe that the C can be removed by heating because the elemental As from the earlier cleaning step tends to protect the GaAs surface.

3:00pm **SC+SS-MoA4 Steady-State Fluctuations of High-T Vicinal Si(111): Investigation of Step-Step Correlation Function of REM Data@footnote 1@*, T.L. Einstein,*** University of Maryland, College Park*; S.D. Cohen,* UM,CP*; J.J. Métois,* University of Aix-Marseilles III, France*; H.G. Bantu,* UM,CP*; H.L. Richards,* Texas A&M University*; E.D. Williams,* UM,CP

To estimate from experimental data the strength of step interactions on vicinal surfaces, one typically studies the terrace-width distribution (TWD), i.e. the separation distance between adjacent steps. From a theoretical perspective, it is simpler to study instead the step-step correlation function h(L), i.e. the probability of finding two steps separated by some distance L, regardless of how many steps lie between them.@footnote 2@ In fact, to the extent that traditional 1+1 D fermion models are applicable, exact results are available for h(L).@footnote 3@ We apply this new approach to extensive REM (reflection electron microscopy) data for the intriguing case of vicinal Si(111) at high temperatures T: 1100, 1200, and 1250°C. To compensate for the sublimation in this regime (e.g. 0.015 ML/s at 1100°C), Si is evaporated onto the sample to maintain steady state.@footnote 4@ Digitizing the data posed several unusual challenges, some of which made this system particularly appropriate for analysis via h(L) rather than TWD. The key question is whether the step stiffness and step-step repulsion of these steady-state systems are consistent with (higher-T extrapolation) of equilibrium results obtained at lower T. @footnote 5,6@ @FootnoteText@ @footnote 1@ Work at UM supported by NSF-MRSEC. @footnote 2@ T.L. Einstein et al., Surface Sci., in press [cond-mat/0012274] & refs. therein. @footnote 3@ P.J. Forrester, J. Stat. Phys.72 (1993) 39. @footnote 4@ S. Stoyanov, J.J. Métois, & V. Tonchev, Surface Sci. 465 (2000) 227. @footnote 5@ H.-C. Jeong & E.D. Williams, Surface Sci. Reports 34 (1999) 171 & refs. therein. @footnote 6@ C. Alfonso, J.M. Bermond, J.C. Heyraud, & J.J. Métois, Surface Sci. 262 (1992) 371.

3:20pm **SC+SS-MoA5 Simplified Bond-Charge Model for the Analysis of Second-Harmonic-Generation Data: Application to Si/Dielectric Interfaces*, J.F.T. Wang,*** *G.D. Powell, R.S. Johnson, G. Lucovsky, D.E. Aspnes,* North Carolina State University

We develop a simplified bond-charge model for the analysis of second-harmonic-generateion (SHG) data, and apply it to study interfaces between singular and vicinal (001) and (111) Si substrates and various oxides, nitrides and oxynitrides. We model SHG microscopically as the 2@omega@t component of dipole radiation generated by the nonsinusoidal motion of electrons in bonds with anharmonic restoring forces, where the bonding electrons are driven by the @omega@t incident field. The simplfying assumption, which makes the treatment of SHG simpler than that of linear optics, is that only the anharmoic polarizability along the bond axis need be considered owing to the expected symmetry of the bond. Using this approach we analyze the azimuthal intensity dependence of SHG in the 800 to 900 nm spectral range of Si interfaces of various orientations and surface terminations. We find for example that a knowledge of the azimuthal dependence of the p-p signal for vicinal (111)Si allows us to predict the p-s, s-p, and s-s signals, and to determine the real and imaginary parts of the nonlinear polarizability associated with the different bonds. For interfaces between vicinal (001) Si samples and thin (less than 10 nm) thermally grown oxides, the essential absence of a 4-fold contribution to the azimuthal intensity dependence shows that these interfaces are double-domain. This result allows us to assign both SHG and RD signals of these interfaces to steps. Differences among oxidized samples and samples nitrided in various ways are relatively small, but systematic.

3:40pm **SC+SS-MoA6 STM Studies of the Ca/Si(111) System***, **J.W. Dickinson**,* Virginia Commonwealth University*; S.C. Erwin,* Naval Research Laboratory*; J.A. Carlisle,* Argonne National Laboratory*; A.A. Baski,* Virginia Commonwealth University

The Ca/Si(111) system forms a series of odd-order nx1 (n = 3,5,7,etc.) reconstructions that culminate with a 2x1 phase at 0.5 ML.@footnote 1@ Similar to group I metals, group II Ca forms a 3x1 phase at low coverage, where a previous model based upon Si honeycomb-chain-channel (HCC) chains accounts well for the observed STM data. In contrast to the group I metals that form the 3x1 phase at 1/3 ML, however, Ca forms this phase at 1/6 ML,@footnote 2@ presumably due to the fact that Ca has twice the number of available electrons. Another interesting behavior unique to Ca is the presence of a 2x1 phase that reaches completion at 1/2 ML. We have proposed a model for the 2x1 phase based upon pi-bonded Seiwatz Si chains, where Ca rows form between the Si chains. The variety of odd-order nx1 phases (5x1, 7x1, etc.) that occur between these end-point 3x1 and 2x1 phases are then appropriate combinations of the 3x1 HCC chains and 2x1 Seiwatz chains. For example, a 5x1 unit cell is composed of one HCC chain and one Seiwatz chain, where two Ca rows are found per unit cell. Calculated surface energies based on the HCC and Seiwatz models correctly predict that for increasing Ca coverage, the 3x1, 5x1, and 2x1 phases each appear as stable phases. @FootnoteText@ @footnote 1@ A.A. Baski, S.C. Erwin, M.S. Turner, K.M. Jones, J.W. Dickinson, J.A. Carlisle, Surf. Sci. 476, 22 (2001). @footnote 2@ G. Lee, D. Shin, J. Koo, H. Kim, S. Hong, Abstract #S25-8, APS 2001 March meeting.

4:00pm **SC+SS-MoA7 Growth of Semiconductor (Si, Ge)/Insulator (CaF@sub 2@) Heterostructures on Si(111)***, **A. Klust**, M. Bierkandt, C. Deiter,* Universität Hannover, Germany*; J. Falta,* Universität Bremen, Germany*; M. Grimsehl,* Universität Hannover, Germany*; R. Feidenhansl, C. Kumpf,* Riso National Laboratory*; T. Schmidt,* Universität Bremen, Germany*; Y. Su,* Universität Hamburg, Germany*; J. Wollschläger,* Universität Hannover, Germany

Silicon-fluorite superlattices exhibit strong photoluminescence at room temperature@footnote 1@. The origin of this novel behavior, not found in bulk silicon, may be electron confinement and/or interface effects. An important contribution to understanding these effects is detailed knowledge of the epitaxial semiconductor/insulator interface structure, which we find to be different for the Si-on-CaF@sub 2@ and CaF@sub 2@-on-Si interfaces. The CaF@sub 2@/Si(111) interface was investigated using x-ray standing wave (XSW) excited photoelectron spectroscopy (XPS). This combination exploits the large binding energy difference between interface and bulk emission to separately locate these sites relative to the Si substrate. The XSW results show that interface Ca atoms are well ordered even at growth temperatures as low as 370°C. Furthermore, we used surface x-ray diffraction (SXRD) to study growth of Si and Ge on thin CaF@sub 2@ films. In contrast to surfactant mediated growth of Si on CaF@sub 2@,@footnote 2@ Si films grown on pristine CaF@sub 2@ films exhibit the same crystallographic orientation as the CaF@sub 2@ film. For the CaF@sub 2@-on-Si interface, the orientation of the substrate and overlayer are rotated by 180° at growth temperatures used here. These differences in interface structure are attributed due to different interface reaction chemistry.@FootnoteText@ @footnote 1@F. Bassani et al., J. Appl. Phys. 79 (1996) 4066. @footnote 2@B. R. Schroeder et al.. Appl. Phys. Lett. 77 (2000) 1289.

4:20pm **SC+SS-MoA8 Structural Relaxation at SiO@sub 2@/Si(100) Interfaces Studied by Coaxial Impact Collision Ion Scattering Spectroscopy***, **H. Ikeda**, S. Goto, K. Honda, M. Sakashita, A. Sakai, S. Zaima, Y. Yasuda,* Nagoya University, Japan

With downsizing the ULSI devices, atomic bonding structures at the SiO@sub 2@/Si interface have become a serious factor to determine the device performance. Nevertheless, there are few studies about the interfacial structure. By using coaxial impact collision ion scattering spectroscopy (CAICISS), we have studied the structural changes extending over the first several layers from oxidized Si(100)-2x1 surfaces and claimed that the inward oxidation occurs before the lateral oxidation finishes.@footnote 1@ In the present study, we clarify Si atomic structures at the SiO@sub 2@/Si interface, which depend on the thickness of the oxide films and the oxidation temperature. An ion scattering simulation which is based on the consecutive calculation of the He@super +@ ion trajectories was used for the analysis of CAICISS spectra. Below an oxide thickness of 2.3 ML, the structural relaxation of a Si lattice at the SiO@sub 2@/Si interface occurs similarly in the range of room temperature to 700°C. The CAICISS spectra show only horizontal displacement of the second-layer Si atoms in these samples. In the following oxidation stage, the oxidation process depends on the temperature. At room temperature, the oxide thickness saturates at 2.3 ML, which is probably due to the restriction of oxygen adsorption on the distorted Si-Si bond sites. The CAICISS spectra of oxidation at above 300°C indicate interface structures that consist of Si atoms existing at normal lattice sites. Furthermore, vertical displacement of the second-layer Si atoms can be detected as well as horizontal one. From these results, it can be concluded that the vertical displacement of the second-layer Si atoms is a trigger of the formation of an amorphous structure and, moreover, a very abrupt SiO@sub 2@/Si interface is realized. @FootnoteText@ @footnote 1@ M. Wasekura, M. Higashi, H. Ikeda, A. Sakai, S. Zaima, Y. Yasuda, Appl. Surf. Sci., 159-160 (2000) 35.

4:40pm **SC+SS-MoA9 Two Dimensional Scattering-images of Lateral Structured GaAs/AlAs Systems as an Example for Diffuse X-ray Scattering at Interfaces***, **J. Stuempel**, I. Busch,* Physikalisch-Technische Bundesanstalt, Germany

Two-dimensional X-ray scattering pattern in reciprocal space (space map) is measured by the reflection of X-rays at grazing incidence. These images are composed of specular and diffuse scattered components. The essential information about the statistical parameters of the interfaces (roughness, correlation length, lateral symmetries, etc.) is contained in the diffuse part of the scattered radiation. As an example of highly structured interfaces we use an GaAs/AlAs multilayer system. The interfaces of a multilayer grown on a substrate with a small miscut (angle about 2 °) between the surface and the (100)-plane reconstructs to a lateral correlated system with step hights of some nanometers. The measured space maps of these systems will be presented in detail. Due to a quantitative data interpretation the results will be compared with numerical simulated data. The simulation is based on a modified scattering theory. The underlaying theory will be presented within the talk.

Semiconductors
Room 124 - Session SC-MoA

GaN Surfaces, Interfaces, and Devices

Moderator: A. Rockett, University of Illinois

2:00pm **SC-MoA1 The Influence of Active Nitrogen Species and Substrate Polarity on the Growth and Doping of GaN Grown by RF Plasma-assisted Molecular Beam Epitaxy***, **T.H. Myers**, A.J. Ptak,* West Virginia University*; L.T. Romano,* Xerox Palo Alto Research Center **INVITED**

Growth of GaN by molecular beam epitaxy (MBE) is typically limited by increased desorption of Ga from the growing surface. We will report on the relative reactivity of the various active nitrogen species produced by rf plasma sources: low and high energy ions, atoms and metastables. Studies of growth rate as a function of temperature suggest the GaN surface is prone to "attack" by neutral and ionic atomic nitrogen above 700oC, promoting decomposition. This leads directly to the observed lower than expected temperature for a significant decrease in growth rate, while this decrease is not observed when the active nitrogen flux consists primarily of nitrogen metastables. Dramatically improved electrical properties are observed in epilayers grown using nitrogen metastables. Similar to most compound semiconductors, GaN lacks inversion symmetry that leads to different chemical terminations on different crystal planes. The two most common surfaces, the (0001) (or Ga-polar) and the (000-1) (or N-polar) surfaces exhibit quite different properties. Results illustrating the differences in basic growth kinetics related to surface polarity will be presented. Surface polarity also has a pronounced influence on doping. A pronounced dependence of Mg incorporation on surface polarity was observed in a series of Mg step-doped epitaxial GaN layers. Measurements indicate surface accumulation of Mg occurs during growth, with stable accumulations of close to a monolayer of Mg on the Ga-polarity surface. This surface layer can cause surface inversion to occur. Beryllium incorporation was also studied for both Ga-polarity and N-polarity GaN. Unlike magnesium, surface polarity-related incorporation differences were less pronounced for Be. Preliminary results, however, indicate a strong dependence of compensation, e.g. point defect formation, on surface polarity. Polarity related issues for O-incorporation will also be discussed.

2:40pm **SC-MoA3 "Functionalizing" the GaN(0001) Surface: The Chemisorption of Organic Amines***, **V.M. Bermudez,*** Naval Research Laboratory

The emergence of "molecular electronics" has led to interest in the synthesis of hybrid organic/semiconductor structures. Surfaces "functionalized" by attachment of unsaturated hydrocarbons provide the possibility of subsequently building complex electro- or photoactive molecular films using, e.g., photochemical or cycloaddition reactions. Previous work@footnote 1@ with NH@sub 3@ shows that amines are highly reactive with the Ga-polar GaN(0001) surface. Here we use mainly XPS, UPS and ELS to study chemisorption of amines involving @pi@-bonded hydrocarbons, focusing on a primary amine (aniline, C@sub 6@H@sub 5@-NH@sub 2@) and a secondary amine (3-pyrroline, C@sub 4@H@sub 6@NH) having N in a 5-member ring with one C=C bond. Dosing near 300 K with either amine causes rapid elimination of the GaN 3.4 eV surface-state loss in ELS and growth of a C=C @pi@-@pi@@super *@ loss at 6.5 eV (aniline) or 7.2 eV (3-pyrroline). The background-corrected xray-excited C KLL and N KLL band areas indicate a saturation coverage of about 0.40 molecules per surface Ga site for either species. In contrast, benzene (C@sub 6@H@sub 6@) does not adsorb under these conditions. HeII UPS shows rich orbital structure, differing from that of either free molecule, which has been analyzed with the aid of ab-initio DFT calculations. The results suggest adsorption via the amine N-atom with the hydrocarbon ring remaining intact. UPS has also been used to measure changes in band bending and in electron affinity (@delta@@chi@) with adsorption. This permits construction of energy-level diagrams showing the alignment of the molecular HOMO and LUMO with the GaN band edges. For aniline (3-pyrroline), the surface dipole layer leads to @delta@@chi@ of about -0.55 (-0.92) eV, vs. the clean-surface @chi@ of 3.3 eV. This large reduction in @chi@ may be useful in electron emission devices. @FootnoteText@ @footnote 1@ V.M. Bermudez, Chem. Phys. Lett. 317 (2000) 290.

3:20pm **SC-MoA5 STM Study of Dislocation-Mediated Surface Morphology of GaN Grown by ECR-Plasma Assisted MBE***, **Y. Cui**, L. Li,* University of Wisconsin

The surface morphology of GaN films grown on the 6H-SiC substrates by ECR-plasma assisted molecular beam epitaxy was studied by reflection high-energy electron diffraction (RHEED) and in situ scanning tunneling microscopy (STM). Clean SiC substrates were prepared by a two-step method of etching in hydrogen atmosphere at 1600 °C and annealing under Si beam in ultrahigh vacuum at 950 °C. These processes remove the polishing damages of the SiC substrates. The resulting surfaces are composed of atomically flat terraces that are separated by triple-layer steps. At temperature between 550 and 600 °C and plasma power of 30 W, two-dimensional growth was observed. The surface morphology of the films can be characterized by two dislocation-mediated structures: pinned steps and spiral hillocks. Straight-pinned steps along the {1120} directions were found for film thickness of 500 Å, created due to the emergence of screw and mixed dislocations at the crystal surface from the bulk of the film. By counting the number of the steps, the dislocation density is estimated to be in the order of 10@super10@ cm@super-2@. At film thickness greater than 1000 Å, these pinned steps grow outward and around the dislocation, forming spiral hillocks with a density in the order of 10@super8@ cm@super-2@. The reduction of the density is explained by annihilation of the dislocations during the formation of the spirals. These results and their implications for GaN epitaxy will be presented at the meeting. This research is supported by NSF DMR-0094105.

4:00pm **SC-MoA7 Search for the Missing Group-III Flux during AlGaN OMVPE***, **J.R. Creighton**, M.E. Coltrin, R.P. Pawlowski,* Sandia National Laboratories

At normal operating conditions, most AlGaN OMVPE reactors exhibit non-ideal behavior with respect to the group-III precursor concentration. The deposition rate can be considerably less than the predicted transport-limited rate, and the solid AlGaN alloy composition is typically a nonlinear function of the gas-phase composition. It is generally thought that gas-phase "parasitic" reactions between trimethylgallium (TMGa), trimethylaluminum (TMAl), and ammonia are responsible for removing group-III material from the deposition process. We have explored many possible mechanisms for the parasitic pathways using both experimental techniques and complex reactive flow simulations. As expected, TMGa and TMAl react with ammonia to form adducts, which we have unambiguously identified with mass spectroscopy and FTIR. We have measured the vapor pressure of the adducts and their mixtures near room temperature and found that physical condensation can be an important process, especially at higher reactor pressures and higher TMAl concentrations. However, over the 0-100°C range we have found no evidence of significant irreversible decomposition reactions, such as methane elimination, which have often been postulated to be the source of the decrease in group-III flux. As the temperature is raised in this range, the adducts simply dissociate back into the original reactants at rates consistent with equilibrium calculations. The lack of evidence for a low temperature parasitic reaction pathway is consistent with our reactive flow simulations, which indicate that the parasitic reaction pathway occurs at high temperatures near the growing surface. The simulations utilized deposition rate measurements from a rotating disk reactor over a wide range of operating conditions chosen to accentuate the differences between possible high-temperature and low-temperature pathways. Recent results examining possible high-temperature pathways will be presented.

4:20pm **SC-MoA8 Models, Concepts and Realizations of Pyroelectronic Heterostructure Devices***, **P. Vogl**, G. Zandler, S. Hackenbuchner, J.A. Majewski, O. Ambacher,* Technische Universitaet Muenchen, Germany*; K. Chu, V. Tilak, R. Dimitrov, L.F. Eastman,* Cornell University **INVITED**

High field transport in semiconductors that possess high internal spontaneous electric fields opens up a new field of "pyroelectronics". The pyroelectric character of group-III-nitrides with wurtzite crystal structure yields a novel degree of freedom in designing and tayloring devices for modern microelectronic applications. We present both theoretical and experimental studies of III-nitride based high electron mobility field effects transistors (HEMT´s) that demonstrate these devices to be optimally suited for high power and high frequency transistors as well as microwave amplifiers. On the theory side, we have employed first principles calculations to determine spontaneous and piezoelectric polarization charges at interfaces and surfaces of GaN based heterostructures and superlattices. Based on this calculated set of electronic structure data, we have performed extensive high field transport simulations for submicron HEMT devices. In addition, we show how the built-in electric fields can be utilized to produce high hole densities as a function of gate voltage in these devices. Experimentally, undoped and pyroelectric AlGaN/GaN HEMT´s have been processed on c-Al@sub 2@O@sub 3@, Si(111) and 6H-SiC substrates that show excellent device characteristics. With gate length down to 150 nm, we have reached an electron transit velocity and intrinsic transit time frequency of 1.3x10@super 7@ cm/s and 106 GHz, respectively, at room temperature. Experimental results for the first microwave amplifier build by a combination of 4x4 AlGaN/GaN HEMTs will be presented.

5:00pm **SC-MoA10 Ni/Au Ohmic Contacts to p-GaN Epilayers***, B. Liu, E. Lambers, **P.H. Holloway,*** University of Florida*; T. Johnson, D. Guiterrez, K. Kidney, W.B. Alexander,* Uniroyal Optoelectronics

The deposition and properties of evaporated thin Ni (5 nm)/Au (5 nm) contacts on MOCVD p-GaN has been studied. After annealing the bi-layer structure in an oxidizing environment, the contact is transformed from a Schottky to an ohmic behavior. The Ni underlying the Au top layer was found to have largely diffused to the surface and formed NiO during the anneal. The Au formed a porous film between the NiO and p-GaN which allowed between 50 and 85% transmission of 450 nm light, depending upon the deposition and annealing conditions. The porous Au network also allowed good sheet resistance with typical values of 300 @ohm@. X-ray photoelectron spectroscopy indicated that the NiO reached to the GaN interface, however a Ni-Ga-Au ternary metallic phase also formed at the interface. This phase modified the capillary forces and resulted in formation of the porous Au network. In the absence of this metallic phase, the Au film broke into islands with a very high sheet resistance. Formation of the porous network will be discussed in terms of a total energy model of thin film morphology. The consequences of forming NiO and forming the ternary metallic layer upon achieving an ohmic contact will also be discussed.

Surface Engineering
Room 132 - Session SE-MoA
Surface Engineering I: Graded, Multicomponent, and Complex Coatings

Moderator: A. Inspektor, Kennametal Inc.

2:00pm **SE-MoA1 Multi-Level Control for Reactive Sputtering**, ***W.D. Sproul***, *B.E. Sylvia,* Reactive Sputtering, Inc.

Pulsed dc power combined with partial pressure control of the reactive gas has made it possible to reactively sputter deposit non-conducting films such as aluminum oxide at relatively high deposition rates. Most reactive sputtering control systems rely on a single feedback signal for process control. However controlling on a single variable can affect the quality and repeatability of the deposited films. For example when the target voltage is used as the feedback signal, it can change for reasons other than a change in the reactive gas partial pressure such as outgassing or a disappearing anode. Another signal is needed to remove the ambiguity in the control process. Similarly if a mass spectrometer is used to provide the primary feedback control signal, the control signal can change with time due to drift in the mass spectrometer. A new system has been built that overcomes the problem of controlling on a single feedback signal. This new system, called IRESS, controls on a primary signal and then makes on-line adjustments to this primary signal based on secondary feedback signals. Examples of how this works for aluminum oxide and aluminum oxynitrides coatings will be given.

2:20pm **SE-MoA2 The Influence of Sputtering Conditions on Microstructure and Mechanical Properties of Zr-Si-N Films Prepared by r.f.- Reactive Sputtering**, ***M. Zhou,*** Osaka University, Japan*; M. Nose,* Takaoka National College, Japan*; Y. Deguchi,* Toyama University, Japan*; T. Mae,* Toyama National College of Technology, Japan*; K. Nogi,* Osaka University, Japan

ZrN and ZrSiN films were prepared in an r.f. sputtering apparatus which has a pair of targets facing each other (referred to as the Facing Target -type r.f. Sputtering). Si content in the ZrSiN films was changed by using different number of Si tips during deposition. Films were deposited on silicon wafer. During the deposition, substrate was heated from room temperature to 473K, 573K and 673K in order to investigate the influence of substrate temperature on the microstructure and properties of transition metal nitride films. The microstructure of the deposited films was studied by XRD. The chemical contents of zirconium, nitrogen and silicon of the films were determined by EPMA with ZAF method. In order to investigate the relationship between mechanical properties and microstructure of films, the hardness and Young's modulus were measured by a nano-indentation system at room temperature. The load was selected to produce an impression depth below 60nm (not more than 5% of film thickness) so that the influence from the substrate can be neglected. The surface morphology of as-deposited films was also observed by AFM. A study of their microstructure and mechanical properties has provided as follows: (1) As-deposited ZrSiN films were consist of nano-crystals and the crystal size was in the range of 5-10 nm; (2) With increasing substrate temperature from room temperature to 673K during deposition, the crystal size of as-deposited ZrSiN films did not show obvious increase; (3) The hardness of ZrSiN films increased with small amount of Si reaching maximum hardness value of 35GPa, regardless of substrate temperature; (4) AFM results show that the surface morphology have obvious change with increasing Si content and substrate temperature.

3:00pm **SE-MoA4 Characterization of Ternary Nitride Films using Spectroscopic Ellipsometry**, ***S.M. Aouadi,*** *T.Z. Gorishnyy,* University of Nebraska - Lincoln*; F. Namavar,* Spire Corporation*; N. Finnegan,* University of Illinois at Urbana-Champaign*; S.L. Rohde,* University of Nebraska - Lincoln

This paper reports on the first attempt to quantitatively analyze the chemical and phase composition of ternary nitride nanocrystalline films using spectroscopic ellipsometry (SE). Coatings of CrBN, TiBN, TiZrN, and TiCrN were deposited at low temperatures (<200 Â°C) on silicon substrates using ion beam assisted deposition (IBAD) and/or unbalanced magnetron sputtering. These coatings were developed for the protective and decorative coating industries, which require very precise compositions to obtain the desired mechanical properties and/or color. The deposited films were characterized post-deposition using x-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), Rutherford Backscattering (RBS), infrared spectroscopic ellipsometry (IR-SE), and visible-light spectroscopic ellipsometry (VIS-SE). The primary phases in the films were identified using XRD. The chemical composition and phase composition of the samples were determined from XPS, AES, and RBS measurements, as appropriate. VIS-SE and IR-SE data were analyzed using two different approaches to obtain the chemical and phase composition of these samples. The first approach relies on the identification of the optical constants for a few samples of known compositions (from RBS, AES or XPS data) and the use of these optical "standards" in the interpolation of the optical constants of unknown materials to deduce the corresponding chemical composition. The second approach is based on the effective medium approximation, which requires the knowledge of the optical constants of each of the constituent phases. The chemical compositions obtained by SE using both the above approaches were compared to the results obtained from traditional chemical analysis techniques (RBS, XPS, and AES).

3:20pm **SE-MoA5 Structural and Chemical Interplays in Hard Coatings Properties: Multinary Transition Metal Nitrides**, ***F. Lévy,*** Swiss Federal Institute of Technology in Lausanne - EPFL, Switzerland*; P. Hones, P.E. Schmid, R. Sanjinés, M. Diserens,* Swiss Federal Institute of Technology in Lausanne - EPFL **INVITED**

Transition metal nitrides are useful as hard, resistant and protective coatings. Both film composition and film morphology have an influence on the functional properties like hardness, wear and corrosion resistance or colour. Physical vapour deposition techniques are flexible enough to allow a control of the chemical and structural characteristics. In turn, targeted or new coating properties can be obtained. In particular new coating chemistries can be explored by reactive sputtering, which is a clean, polyvalent process, compatible with elemental metal sources. Property improvements may be driven by structural and morphological features, as discussed for example in (CrMo)N ternary sputtered thin films. In contrast, the effects of electronic structure and chemical bonding are illustrated in (CrW)N. In single-phase refractory thin films, the hardness often increases with increasing substrate temperature T@sub s@. This effect has been related to an increase of the grain size d (e.g. in TiN, H@sub m@ = 23...35 GPa with d = 300...600 nm for T@sub s@ = 200...650 @degree@C). In CrN@sub y@, however, the increase in hardness from 8 to 19 GPa observed with increasing substrate temperature T@sub s@ = 330...680 @degree@C was not related to the grain size in a straightforward manner. For this material the grain size was always of the order of 40 nm. The porosity of the film, however, was reduced by substrate heating as demonstrated by an increase of the density. In the ternary compounds, for example in Cr@sub 1-x@Mo@sub x@N@sub y@, the grain size increases significantly in comparison with the binary end compounds. This grain size increase is accompanied by a loss of hardness. The morphology of the films remains columnar and the apparently increasing porosity can be held responsible for the deterioration of the mechanical properties. The chemical composition is determining for most properties, even if often masked by the morphological features. Such effects are present in binary compounds (CrN@sub y@) and are amplified in ternary systems ((Cr,M)N@sub y@ with M = Mo, W).

4:20pm **SE-MoA8 Formation of Voids and its Influence on the Thermal Stability of Co Silicide**, ***N.S. Kim,*** *H.S. Cha, N.G. Sung, H.H. Ryu, W.G. Lee,* Hynix Semiconductor, Korea

We investigated the voids formation during Co silicidation and its influence on the thermal stability of CoSi@sub 2@ on boron or BF@sub 2@-doped poly-Si in ULSI device. The sheet resistance of as-formed CoSi@sub 2@ has been slightly higher on BF@sub 2@ doped poly-Si than boron doped poly-Si, but the sheet resistance of CoSi@sub 2@ on boron doped poly-Si after thermal process increased abruptly. Cross-sectional TEM has shown local voids at the interface between CoSi@sub 2@ and BF@sub 2@ doped poly-Si, but no void on boron doped poly-Si. Furthermore, as pre-cleaning time in diluted HF before Co deposition increased, sheet resistance of as-formed CoSi@sub 2@ decreased and void formation on BF@sub 2@ doped poly-Si was suppressed, but thermal stability of CoSi@sub 2@ after following thermal process was aggravated. From those results, It was thought that the thermal agglomeration of CoSi@sub 2@ was suppressed by stress release at the interface with local voids formed by remained oxide and some florine compounds on the surface of BF@sub 2@ doped poly-Si.

Surface Science
Room 120 - Session SS1-MoA
Innovations in Surface Science

Moderator: U. Heiz, University of Ulm, Germany

2:20pm **SS1-MoA2 An Accurate Paremetrization for the Extended Hückel Theory (EHT): Application to the Electronic Structure and STM Imaging of the Cu(110)+c(2x2)-Si Surface Alloy***, **J.I. Cerdá**, C. Rojas, C. Polop, J.A. Martin-Gago,* Instituto de Ciencia de Materiales de Madrid, CSIC, Spain*; R. Fasel, J. Hayoz, D. Naumovic, P. Aebi,* Universite de Fribourg, Switzerland

The electronic structure of the Cu(110)+c(2x2)-Si surface alloy has been studied both experimentally and theoretically. On the experimental part, we have mainly employed Angle Resolved Ultraviolet Photoemission Spectroscopy (ARUPS) together with atom resolved images acquired with a Scanning Tunneling Microscope (STM). On the theoretical part, we have made use of a recently developed Extended Hückel Theory (EHT) parametrization scheme@footnote 1@ in order to describe the Atomic Orbital (AO) interactions, while the Cu(110)+c(2x2)-Si system has been modelled by a surface-alloy layer stacked on top of a semi-infinite Cu(110) bulk. The corresponding electronic structure and associated STM images (for different tips) have been calculated via Green's functions techniques. Despite the simplicity of the EHT approach, we find a very good agreement with the surface specific electronic features experimentally observed: Fermi surface, Surface State Bands, Atomic corrugation in the STM images, etc. This fact evidences the good transferability of the EHT parameters between different chemical and geometrical environments. @FootnoteText@ @footnote 1@J. Cerdá and F. Soria, Phys. Rev. B, Vol. 61 (2000) 7971.

2:40pm **SS1-MoA3 UV Free Electron Lasers and Their Applications in Surface Science***, **M. Marsi**,* Sincrotrone Trieste, Italy **INVITED**

Free Electron Lasers (FELs) are intense, monochromatic, tunable and coherent light sources that, thanks to their unique features, are opening new research opportunities in many different fields. For several years FEL's have been operating with success in the infrared; recently a considerable progress has been made in the UV region, where lasing wavelengths shorter than 190 nm have been able to be obtained, disclosing new opportunities for the study of the electronic properties of thin films and microstructures. UV FEL's are powerful instruments to probe the excited states of matter, especially when used in combination with synchrotron radiation in a pump-probe configuration. This kind of two-photon photoemission experiments, performed on Si surfaces and interfaces, have allowed a detailed study of the behavior of the non-equilibrium carrier distribution, making it possible to observe the role of interface states in the charge flow mechanism at photoexcited surfaces. Beside their use in combination with synchrotron radiation, UV FEL's have some unique features which make them particularly attractive also per se: in particular, being very intense and naturally tunable, they are ideal light sources for threshold photoelectron emission microscopy, and thus powerful instruments to study the electronic properties of nanostructures.

3:20pm **SS1-MoA5 An End Station for Synchroton-Based Photoelectron Spectroscopy of Actinide and Other Highly Reactive Samples***, D.A. Arena, **J.G. Tobin**,* Lawrence Livermore National Laboratory*; D. Shuh,* Lawrence Berkeley National Laboratory*; R.K. Schulze,* Los Alamos National Laboratory*; P. Boyd,* Boyd Technologies, Inc.

We have constructed a specialized UHV experimental chamber to allow for the convenient study of the electronic structure of actinide and other highly reactive samples using synchrotron radiation at the Advanced Light Source (ALS). This chamber, the Actinide Spectroscopy End Station (ASES), is currently equipped to perform high-resolution photoemission spectroscopy in both spin integrated and spin resolved modes. The system includes a novel sample introduction system where samples are brought on-site in small ion-pumped vacuum suitcases and introduced into the experimental chamber without exposure to the atmosphere. We have included a separate sample preparation chamber to provide for sample cleaning and gas dosing followed by a quick transport to the analysis position. The ASES is equipped with numerous isolation valves to allow for the removal and repair of individual components while maintaining the vacuum integrity of the overall system. The sample manipulator allows for both heating and liquid nitrogen cooling of the samples and the end station also contains a number of redundant systems such as multiple sample heating and temperature measurement stages so that experiments can continue in the event of common occurrences such as a broken heating filament or open thermocouple connection. Expansion plans include the addition of a fluorescence spectrometer and a thin film deposition system. An extensive series of experiments are planned, including resonant photoemission, spin-resolved double polarization investigations, and oxidation studies of elemental plutonium and other actinide samples. This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

3:40pm **SS1-MoA6 Closing the Pressure Gap: Photoemission at 5 Torr and the Premelting of Ice***, **D.F. Ogletree**,* Lawrence Berkeley National Laboratory*; H. Bluhm,* Lawrence Berkeley National Lab and Fritz Haber Institute, Germany*; F. Requejo,* Lawrence Berkeley National Laboratory*; C.S. Fadley,* Lawrence Berkeley National Lab and University of California at Davis*; Z. Hussian, M. Salmeron,* Lawrence Berkeley National Laboratory

Fundamental studies of surface processes and reactions at high pressure are outside the reach of many surface science techniques - the so-called "pressure gap". Scanning probe microscopy and non-linear optical probes can be used to study surface topography and vibrational excitations, respectively, but probes of electronic structure and atomic composition are hard to come by. We have recently extended x-ray photoemission spectroscopy to pressures as high as 5 Torr using a synchrotron light source and a differentially pumped electron transfer lens. One of the first applications of this method has been a study of the pre-melting of the ice surface. The new instrument will be described, and the results on ice pre-melting will be presented. Near-edge x-ray adsorption fine structure (NEXAFS) probes the density of unoccupied molecular states. In the case of water, NEXAFS is sensitive to the effects of hydrogen bonding and can therefore distinguish between water vapor, liquid water and ice. Surface sensitivity was obtained by using the O KLL Auger electron yield as a probe of x-ray absorbtion. Electron spectroscopy allowed the Auger yield to be extracted, since total electron yield measurements were complicated by secondary electron cascades in the gas phase. Pre-melting was investigated for ice, in equilibrium with its vapor, between -40 and 0 C (the vapor pressure of ice at the melting point is 4.6 Torr). NEXAFS results showed that a liquid-like film exists at the ice surface above -20 C, reaching a thickness of ~ 2 nm near 0 C. We also found that the presence of hydrocarbon contamination strongly influenced the pre-melting of ice.

4:00pm **SS1-MoA7 Desorption/Ionization on Porous Silicon (DIOS) Mass Spectrometry: A New Methodology for Bioanalysis***, **Z. Shen**, J.E. Crowell,* University of California, San Diego*; G. Siuzdak,* The Scripps Research Institute

DIOS-MS is a new mass spectrometry strategy based on pulsed laser desorption/ionization from a porous silicon surface. DIOS-MS is similar to matrix-assisted laser-desorption ionization mass spectrometry (MALDI-MS) in that it utilizes the same instrument; however, in DIOS-MS, porous silicon is used to trap analytes deposited on the surface and laser radiation is used to vaporize and ionize these molecules, without the presence of any matrix material. We have shown that DIOS-MS can be used for a wide range of small molecules as well as biomolecules at the femtomole and attomole level with little or no fragmentation, in contrast to what is typically observed with other direct desorption/ionization approaches. DIOS-MS offers many unique advantages including good sensitivity, low background ion interference, and high salt tolerance. We will demonstrate the application of DIOS-MS to small molecule quantitative analysis, chemical reaction monitoring, enzyme-substrate reaction and inhibition characterization, and drug metabolism study. We will also demonstrate DIOS-MS as a unique scanning approach for small-molecule high throughput analysis.

4:20pm **SS1-MoA8 Enantiospecific Properties of Chiral Surfaces***, **J.D. Horvath**, A.J. Gellman,* Carnegie Mellon University

Chirality is an omnipresent feature of the biochemical and biophysical world. The handedness of the important molecules that form the basis of life creates the need for enantiomeric purity in the chemicals used for pharmaceutical and other bio-active purposes. Many of the processes used for synthesis and preparation of enantiomerically pure compounds rely on the use of chiral surfaces. This represents in interesting and important new opportunity for surface science. I will describe some of the recently discovered, enantiospecific physical and chemical properties of chiral surfaces prepared from simple high Miller Index metal surfaces. The kinked step structures of such surface are chiral. As an example, the heats of adsorption of small chiral molecules such as propylene oxide (CH@sub 3@CH(O)CH@sub 2@) and R-3-methylcyclohexanone are sensitive to the handedness of surfaces such as Cu(643). This has been observed using thermally programmed desorption measurements which reveal that the desorption kinetics of these chiral molecules are enantiospecific on chiral surfaces. They do not exhibit enantiospecificity on achiral surfaces such as Cu(111). Similarly, the orientation of chiral molecules on chiral surfaces can be shown to depend on the relative handedness of adsorbate and substrate. This has been shown by study of the infrared reflection absorption spectra of 2-butanoxy groups on the Ag(643) surface. The intensities of the absorptions by R- and S-2-butanoxy groups are dependent on the handedness of the Ag(643) substrate. Understanding and controlling these enantiospecific properties poses some extremely interesting challenges for surface chemistry and surface physics that can have broad impact in the chemical and life sciences.

4:40pm **SS1-MoA9 Can Cu-TBP Porphyrin Molecules Emit Light under an STM Excitation?**, *D. Fujita, H. Nejo, S. Yokohama, S. Mashiko, **Z.-C. Dong**,* National Institute for Materials Science, Japan

Photon emission on metal surfaces induced by tunneling electrons is thought to arise from the radiative decay of localized surface plasmons. While this theory is still not yet complete due to the negligence of non-local effects, the situation becomes more complicated and difficult to study when molecules are sandwiched between the tip and surface. It remains unclear how molecules couple with the electrodes and electromagntic field to give out light. We demonstrate here a technique to produce tunneling-electron induced photon emission from Cu-TBP porphyrins on Cu(100). The emission intensity and optical spectra show not only the enhancement effects, but also new features revealing the molecular origin of light emission. The quantum efficiency is estimated to be 10@super -4@ photons per electron. The observation of a broad peak around 630 nm associated with molecules is particularly exciting but puzzling, since Cu-centered porphyrin molecules are known not to fluoresce under photoexcitation. This broad peak appears dramatically enhanced when the bias voltage is above 3 V, in good agreement with the high B-band absorption via optical excitation. These observations suggest that while energy absorption behavior by electrons appears in parallel with that by photons, the excitation or decay mechanism might be different in the two processes, and may thus bring up new physics. Tunneling electrons can excite surface plasmons in metal substrates, which causes the enhancement of local electromagnetic field. Excitation of molecules occurs via the resonant coupling of molecular electronic states with the localized electromagnetic modes between the tip and substrate. Light is emitted when excited molecules decay to the ground state. The decoupling of luminescent porphyrin cores from the substrate, a means to suppress the fast nonradiative energy dissipation, is found to be important for efficient light emission.

5:00pm **SS1-MoA10 A Fourier Transform-Based TOF HREELS Spectrometer**, *R.H. Jackson, L.J. LeGore, Y. Yang, P. Kleban, **B.G. Frederick**,* University of Maine

A major limitation of the conventional, dispersive sector, electron energy analyzer is that it is inherently a serial device, leading to long data acquisition times in high resolution electron energy loss spectroscopy (HREELS). A throughput advantage of order 500-1000 can be achieved by combining time-of-flight (TOF) methods with pseudo-random (PRBS) modulation of the back-scattered electron beam. We present the first results of this new approach to HREELS and compare with simulations of the TOF spectrometer. Although PRBS modulation techniques have been applied to a number of other areas,@footnote 1,2@ the Poisson noise distribution arising from pulse-counting detection and the sub-nanosecond time resolution required for meV resolution in HREELS place several demands upon the chopper, detection electronics and digital signal processing software. We will discuss how the chopper, based upon the "interleaved comb" device,@footnote 3@ limits the minimum gating time and the nominal time resolution of the spectrometer. Traditional cross correlation methods, utilized to recover the signal in PRBS modulation, obtain a throughput advantage over single pulse TOF at the expense of resolution; however, the methods are not strictly valid when the noise correlates with signal power. To overcome these limitations, we have developed maximum likelihood methods which account for the Poisson noise distribution and achieve a resolution enhancement of up to a factor of 8, relative to the nominal TOF time resolution, depending upon the signal to noise ratio. @FootnoteText@ @footnote 1@ Y. Uehara, T. Ushiroku, S. Ushioda, Y. Murata, Jap. J. App. Phys., 29 (1990) 2858-2863. @footnote 2@ J. L. Buevoz, G. Roult, Rev. de Phys. Appl., 12 (1977) 59 7. @footnote 3@ P. R. Vlasak, D. J. Beussman, M. R. Davenport, C. G. Enke, Rev. Sci. Instrum., 67 (1996) 68-72.

Surface Science
Room 121 - Session SS2-MoA
Molecular Interactions with Oxide Surfaces

Moderator: U. Diebold, Tulane University

2:00pm **SS2-MoA1 Probe Molecules on Hydroxylated @gamma@-Al@sub 2@O@sub 3@/NiAl(100): Characterization of Surface OH Acidity**, ***K.A. Layman**, J.C. Hemminger,* University of California, Irvine

Hydroxylated thin films of @gamma@-Al@sub 2@O@sub 3@ are grown by exposing a NiAl(100) single crystal to 100 L H@sub 2@O at 1000 K. In HREELS analysis, these films exhibit the phonon modes in agreement with @gamma@-Al@sub 2@O@sub 3@ films grown on the NiA l(100) substrate using 2400 L O@sub 2@ at 1000 K. In addition to the observed phonon modes, a single OH stretch is observed at 3270 cm@super -1@ (FWHM approximately 100 cm@super -1@). This frequency is indicative of non-interacting OH groups bonded to 2 or 3 Al atoms. To characterize the acidity of the surface OH groups, we have studied the adsorption of probe molecules, such as pyridine, benzene, and toluene, on the hydroxylated @gamma@-Al@sub 2@O@sub 3@ surface at 150 K. The probe molecules, acting as bases, form acid-base complexes with the surface OH groups. HREELS spectra were recorded as a function of probe molecule coverage. Complex formation causes the OH bond strength to decrease and the OH stretch to shift to lower frequency. The adsorption and complex formation is observed to be reversible. The OH frequency shift is dependent on the probe molecule basicity and the OH acidity. Our results indicate that two types of isolated OH with different acidity exist on the surface. The correlation between OH frequency shift and probe molecule basicity allows us to determine the acid strength of the surface OH groups quantitatively.

2:20pm **SS2-MoA2 Evidence for a Radical-Radical Reaction between O@sub 2@ and OH on TiO@sub 2@(110)**, ***M.A. Henderson**, C.L. Perkins,* Pacific Northwest National Laboratory

Water readily dissociates at oxygen vacancy sites on TiO@sub 2@(110) to form bridging OH groups.@footnote 1-3@ These OH groups exhibit properties that are more consistent with what one would expect from OH radicals rather than from OH@super -@ ions. A surface consisting solely of these OH groups is easily prepared by adsorption of a multilayer water exposure at 130 K followed by heating to 300 K to desorb all molecular water. Recombination of the bridging OH groups occurs in a TPD peak at about 500 K. ELS spectra of the 10% vacancy-covered surface before and after exposure to water both possess the 0.8 eV loss feature attributable to Ti@super 3+@ cations. The inability of water/OH to oxidize Ti@super 3+@ cations at vacancy sites is consistent with earlier photoemission studies.@footnote 4@ In contrast, this ELS feature is absent after O@sub 2@ exposure at RT due to oxidation of the vacancies. Surprisingly, exposure of O@sub 2@ to bridging OH groups results in replacement of the 500 K recombinative desorption state of water with a sharp H@sub 2@O TPD state at 300 K. Concurrent with this change, the Ti@super 3+@ cations are oxidized and O adatoms are deposited on the surface. We speculate that the most likely explanation for this behavior is a radical-radical reaction between O@sub 2@ and OH. Such a reaction does not occur between OH groups and diamagnetic molecules like CO@sub 2@.@footnote 5@ These findings suggest that bridging OH groups on TiO@sub 2@(110) formed from the dissociative adsorption of H@sub 2@O at vacancy sites might be useful in exploring the thermal chemistry OH radicals believed to be formed on TiO@sub 2@ photocatalysts. @FootnoteText@ @footnote 1@. M.B. Hugenschmidt, et al., Surf. Sci. 302 (1994) 329. @footnote 2@. M.A. Henderson, Langmuir 12 (1996) 5093. @footnote 3@. W.S. Epling, et al., Surf. Sci. 412/413 (1998) 333. @footnote 4@. R.L. Kurtz, et al., Surf. Sci. 218 (1989) 178. @footnote 5@. M.A. Henderson, Surf. Sci. 400 (1998) 203. R.

2:40pm **SS2-MoA3 Sulfur Adsorption and Reaction with a TiO@sub 2@(110) Surface: O - S Exchange and Sulfide Formation**, ***J. Hrbek**, J.A. Rodriguez, J. Dvorak, T. Jirsak,* Brookhaven National Laboratory

Upon sulfur adsorption on TiO@sub 2@(110) at 600 K all surface oxygen is replaced by S. High-resolution photoemission data show a complete loss of oxygen from the surface layer, a large binding energy shift and attenuation of Ti core levels, and the presence of three different S species. The bonding of sulfur is examined using first-principles density-functional calculations and the periodic supercell approach. At saturation the top layer of the oxide surface is converted to sulfide, with the majority of sulfur buckled above the Ti lattice plane and the remaining sulfur bonded in bridging sites. A mechanism for this self-limiting thermodynamically unlikely surface reaction is proposed. This research was carried out at Brookhaven National

Laboratory under contract DE-AC02-98CH10086 with the US Department of Energy (Division of Chemical Sciences).

3:00pm **SS2-MoA4 Molecular Adsorbate Geometries and Bondlengths on NiO(100); A Failure of Current DFT Theories***, **M. Kittel,** J.-T. Hoeft, M. Polcik,* Fritz-Haber-Institut der MPG, Germany*; R.L. Toomes, J.-H. Kang,* University of Warwick, UK*; M. Pascal, C.L.A. Lamont,* University of Huddersfield, UK*; D.P. Woodruff,* University of Warwick, UK

Current density-functional theory has been shown to be extremely successful in reproducing the local geometries and bondlengths of adsorbates on metal surfaces, for which there is a significant body of experimental data. In the case of oxide surfaces, however, there is a dearth of experimental structural data to compare with the results of such theory. Here we present the results of quantitative structure determinations for new studies of CO and NH@sub3@ on NiO(100) epitaxial films using photoelectron diffraction in the scanned-energy mode (PhD) combined with full multiple scattering simulations. Both species, like NO which we studied previously, occupy sites atop surface Ni atoms, with bondlengths which are slightly longer than we have found for the same species on metallic Ni surfaces, but much shorter (by up to 0.79 Å) than predicted by theory. The results highlight a major failure of current theory to provide an adequate description of molecule/oxide bonding, which was previously only evident through a comparison of experimental thermal desorption data with theoretical bonding energies. A comparison of the molecule-Ni nearest neighbour bondlengths for these singly-coordinated sites on NiO(100) with those found on metallic Ni(111) shows that while the bondlengths on the oxide surface are systematically longer than on the metal surface, these effects are far more subtle than those reflected by current theoretical treatments.

3:20pm **SS2-MoA5 The Stability of Polar Oxide Surfaces and Their Interaction with Deposits***, **C. Noguera,*** CNRS, France*; J. Goniakowski,* CRMC2, France*; F. Finocchi,* Laboratoire de Physique des Solides, France **INVITED**

It has long been recognized that the most interesting or active surfaces for the applications are not necessarily the most perfect ones. In insulating oxides, geometric defects, nanofacets, or stoichiometric defects are usually associated to specific electronic states located in the forbidden gap region, which confer a higher reactivity to the surfaces. From this view point, polar oxide surfaces are of prominent interest: their intrinsic instability, due to the existence of a non-zero dipole moment in the repeat unit perpendicular to the surface, may be overcome by a deep modification of the surface electronic structure --- total or partial filling of surface states, sometimes leading to surface metallization --- or by strong changes in the surface stoichiometry --- spontaneous desorption of atoms, faceting, large-cell reconstructions, etc. We will examine several of these issues, through the results of first principles simulations of the MgO(111) surface, based on the density functional method. We will discuss the relative stability of various surface reconstructions, in relation with recent grazing incidence X Ray diffraction and atomic force microscopy experiments. The mechanism by which is achieved the charge compensation necessary to heal the polarity when transition metal atoms are deposited on the surface will be described and the trends in the adhesion energy along the transition series will be discussed. Finally we will present recent results on the dissociation of water on MgO(111).

4:00pm **SS2-MoA7 Small Molecule Adsorption on SrTiO@sub 3@ and CaTiO@sub 3@ Surfaces***, **K.F. Ferris,*** Pacific Northwest National Laboratory, us*; L.-Q. Wang,* Pacific Northwest National Laboratory

Interactions of water and formate with stoichiometric and defective on (001) MTiO3 surfaces (M=Ca, Sr) have been studied using semiempirical and first principles electronic structure calculations. Preliminary results for water interaction with (001) CaTiO 3 indicate weaker adsorption than TiO2 surfaces, consistent with experimental results. Though energetically similar, water adsorption on TiO2- and CaO-terminated CaTiO3 surfaces result in a distinctly different geometric arrangements due to the surface ox ygen atoms and the charge distribution of these acceptor sites. Stepped (001) CaTiO3 surfaces have oxygen sites with greater accessibility and lower coordination, and are predicted to have increased reactivity for H2O and HCOOH. Preliminary results for fo rmate interaction with (100) SrTiO3 indicate strong adsorption consistent with experimental results, but in a distinctly different geometric arrangement from the TiO2 surfaces due to absence of bridging oxygen sites. Further results will be discussed in terms of potential reaction mechanisms and correlations with ongoing experimental studies. This work was supported by the U.S. Department of Energy, Office of Science, Material Sciences Division, under contract DE-AC06-76RLO 1830.

4:20pm **SS2-MoA8 Dramatic Cooperative Effects in Chemisorption of NO@sub x@ on Oxide Surfaces***, **W.F. Schneider,*** Ford Research Laboratory*; M. Miletic,* University of Michigan*; K.C. Hass,* Ford Research Laboratory*; J.L. Gland,* University of Michigan

NO@sub x@ adsorption by base metal oxide sorbents is central to numerous NO@sub x@ aftertreatment technologies, including those essential to enabling fuel-efficient "lean burn" combustion for transportation applications. While the ability of base metal oxide surfaces to form surface nitrites and nitrates is well established by TPD, XPS, and IR experiments, the identity and mechanisms of formation of the adsorbates are not well understood, inhibiting attempts to design oxides with more useful adsorption properties. In this work, first-principles DFT calculations are used to study NO@sub x@ adsorbates on alkaline earth oxide surfaces. We show that isolated NO or NO@sub 2@ are weakly physisorbed to these surfaces, but that adsorption is strongly enhanced by the formation of adsorbate pairs. This remarkable and unprecedented cooperative chemisorption phenomenon is a consequence of the amphoteric character of NO and NO@sub 2@ and the acidity and basicity enhancements possible when charge is transferred between two adsorbates. These results provide a novel and consistent picture of oxide surface nitrition and nitration and are a key step along the path of rationally designed NO@sub x@ adsorbants.

4:40pm **SS2-MoA9 CO@sub 2@ and BF@sub 3@ Adsorption on Cr@sub 2@O@sub 3@ (1012): Probing Surface Basicity and Oxygen Anions***, M.W. Abee, **D.F. Cox,*** Virginia Polytechnic Institute & State University

The basic properties of oxide surfaces are often associated with surface lattice oxygen anions. CO@sub 2@ is the standard probe molecule for investigating surface basicity, but little information is available in the surface science literature concerning its interaction with well-defined (single crystal) oxide surfaces. On Cr@sub 2@O@sub 3@ (1012), CO@sub 2@ interacts primarily with cation/anion site pairs to form bidentate carbonates that are stable at room temperature. These sites are associated with five-coordinate Cr@super 3+@ cations on the stoichiometric, non-polar (1012) surface. Terminating the surface cations with chromyl oxygen (Cr=O) via dissociative O@sub 2@ chemisorption breaks the interaction and gives rise to a weakly-bound CO@sub 2@ moiety. BF@sub 3@, a strong Lewis acid, interacts directly with anions on the stoichiometric surface, giving a surface/adsorbate complex stable to above room temperature. However, unlike CO@sub 2@, BF@sub 3@ forms a more stable complex with chromyl oxygen on the oxide-terminated surface. The results demonstrate that thermal desorption experiments with BF@sub 3@ provide a means for probing the Lewis basicity of surface oxygen anions of different coordination.

5:00pm **SS2-MoA10 Synchrotron X-ray Photoelectron Studies of the CCl@sub 4@ Chemistry on Fe@sub 3@O@sub 4@ (111)- 2x2 Surfaces***, **K. Adib**, N. Camillone III, J.P. Fitts, Z. Zhu, R.M. Osgood, Jr.,* Columbia University*; S.A. Joyce,* Pacific Northwest National Laboratory*; D.R. Mullins,* Oak Ridge National Laboratory

We have used synchrotron x-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD) to investigate the reactions of CCl@sub 4@ with Fe@sub 3@O@sub 4@ (111) surfaces. Natural single crystals of @alpha@-Fe@sub 2@O@sub 3@ were cut and polished in the (0001) orientation. They were processed in ultrahigh vacuum to produce a surface selvedge of Fe@sub 3@O@sub 4@ (111)- 2x2 and exposed at ~100 K to CCl@sub 4@. TPD results indicate a highly reactive surface in which the dissociation of CCl@sub 4@ into Cl and CCl@sub 2@ plays an important role. XPS results confirm the presence of three Cl-containing species immediately upon dosing. The data is consistent with presence of unreacted CCl@sub 4@, and chemisorbed CCl@sub 2@ and Cl on the surface. We propose that upon subsequent heating of the surface, the chemisorbed species can (1) abstract an oxygen and desorb as OCCl@sub 2@, (2) associatively desorb as C@sub 2@Cl@sub 4@ or (3) recombinatively desorb as CCl@sub 4@. We have observed differences in the TPD spectra following the initial dosing of the surface as compared to those following subsequent dosings. These marked changes in the surface are explained in terms of incomplete desorption of iron chloride and carbon species upon heating as verified by XPS. At sufficiently high dosages of CCl@sub 4@, the iron chlorides formed on the surface consisted of multiple species, possibly FeCl@sub 2@ and FeCl@sub 3@.

Thin Films
Room 123 - Session TF+NS+SE+VST-MoA

Nanophase & Multilayered Thin Films

Moderator: E. Majkova, Institute of Physics SAS

2:40pm **TF+NS+SE+VST-MoA3 Precision Multilayered Thin Films for Manufacturing of the Next Generation of Computer Chips**, *E Spiller,* Lawrence Livermore National Laboratory **INVITED**

Lithographic cameras for the fabrication of circuits below 70 nm line width can not use lenses because no transparent material exists for the required short wavelengths in the ultraviolet. Extreme Ultraviolet (EUV) lithography with wavelengths around 13 nm using multilayer coated mirrors is a main contender for chips with line widths between 30 and 70 nm. Meeting the one Angstrom tolerances on the figure and smoothness of the optical surfaces before and after the multilayer deposition and controlling the profile of the multilayer period to better than 0.1 Angstrom has been a major challenge. The talk will give an update on the status of EUV lithography with emphasis on the fabrication, characterization and understanding of the required film deposition processes.

3:20pm **TF+NS+SE+VST-MoA5 Ion Beam Growth and Properties of SiN/TiN Multilayer Thin Films for Phase-shift Masks in Optical Lithography**, ***P.F. Carcia,*** *M.H. Reilly,* DuPont Central Research and Development; *L.J. Pilione, R.F. Messier,* Pennsylvania State University; *L. Dieu,* DuPont Photomask; *R.S. McLean,* DuPont Central Research and Development

Today's high speed microprocessors and dense memory chips are the result of modern optical lithography that allows printing smaller and smaller circuit features on a Si wafer. In 2002, optical lithographic tools with imaging radiation of 193 nm will produce leading edge devices with sub 100 nm critical dimensions. The continued success of optical lithography, which has delayed the introduction of next generation technologies with X-rays, ions, or electrons, can be attributed to the innovative application of optical resolution enhancement techniques that improve feature resolution and increase process latitude. One of these, the attenuating phase-shift mask (attPSM) improves image contrast with destructive optical interference by transmitting (6-17%) and simultaneously phase-shifting 180 degrees imaging radiation through the mask. In this paper we describe a systematic approach for designing wavelength tunable (248nm to 157 nm) attPSMs with SiN/TiN multilayers. We grew these multilayers by dual ion beam deposition (IBD) because it is potentially a cleaner process than magnetron sputtering. Compared to SiN/TiN multilayers grown by magnetron sputtering, IBD produced films with smaller surface roughness (AFM), less chemical contamination (XPS), and flatter interfaces (XRD, TEM). However, IBD films had higher stress, which can cause distortion of the mask and consequent image placement errors. We have therefore investigated strategies, which will also be discussed, to reduce stress in ion beam sputtered SiN/TiN multilayers.

3:40pm **TF+NS+SE+VST-MoA6 Gold Nanoparticle Films via Inert Gas Deposition: Biased Percolation and Current Induced Organization During and after Deposition**, ***L.B. Kish,*** *P. Chaoguang, J. Ederth,* Uppsala University, Sweden; *W.H. Marlow,* Texas A&M University; *C.G. Granqvist,* Uppsala University, Sweden **INVITED**

Gold nanoparticle films made by inert gas deposition have been attracting attention due to their super hardness and thermal stability, which make the films promising objects for future microelectronics applications. The exact origin of the superior proper ties is unknown and to learn the conditions for optimal properties, strong efforts have been made. The published investigations have been made after the films were deposited. This talk reports a different way of study: measuring the electrical conductivit y during deposition. During the measurement, various electrical fields have been applied in order to test the possible influence of the measuring current on the film formation. The time dependence of the conductivity showed various rich patterns including local maximums/minimums. The exact interpretation of the whole process is yet to be make, however, it is possible to make a phenomenological picture of the origin of the observed current-induced-organization phenomena, which include elements of: - Biased percolation: conductor-insulator transition; - Biased percolation: bad conductor - good conductor transition; - Annealing; - Sintering; - Electromigration. A possible technological application of the observed phenomena is the fabrication of nanoparticle films with controlled disorder, such as, fine tuning of chemical sensors.

4:20pm **TF+NS+SE+VST-MoA8 Deposition of Metallic Nanoclusters by Galvanic Displacement**, ***L. Magagnin,*** Politecnico di Milano, Italy; *C. Carraro, R. Maboudian,* University of California at Berkeley

Wet processes for the deposition of metallic films on silicon from fluoride containing solution are currently under investigation,@footnote 1,2@ for applications in microelectronics and in micromechanical systems technology. This work presents a novel method for depositing nanostructured films of noble and platinum-group metals by galvanic displacement from water-in-oil microemulsions. One possible application of this process is coating of the interior walls of microchemical reactors@footnote 3@ for enhanced catalytic activity. The water-in-oil system investigated comprises an organic phase (n-heptane), a surfactant (AOT), and an aqueous solution of hydrofluoric acid and metallic ions. Metallic nanoclusters are deposited by galvanic displacement at the silicon substrate in contact with the fluoride containing water droplets. Nanoclusters with controlled size and distribution are obtained on silicon by regulating the micellar radius and deposition time. Scanning probe microscopy is employed to characterize the deposited films. Microscopic observations are correlated with X-ray diffraction and SEM/EDS analyses to investigate the nucleation and growth of the nanoclusters. @FootnoteText@ @footnote 1@M.K. Lee, J.J. Wang, H.D. Wang, J. Electrochem. Soc. 144, 5 (1997): p. 1777. @footnote 2@L. Magagnin, R. Maboudian, C. Carraro, Electrochemical and Solid-State Letters 4, 1 (2001): p. C5. @footnote 3@K.F. Jensen, "The impact of MEMS on the chemical and pharmaceutical industries", Solid-State Sensor and Actuator Workshop, Hilton Head Island, South Caroline, June 4-8 (2000): p. 105.

4:40pm **TF+NS+SE+VST-MoA9 Cross-Linked Nano-Onions of Carbon Nitride in Thin Solid Films**, ***L. Hultman,*** *S. Stafstrom, Zs. Czigany, J. Neidhardt,* Linköping University, Sweden; *N. Hellgren,* University of Illinois at Urbana-Champaign; *I.F. Brunell,* Linköping University, Sweden; *K. Suenaga,* Meijo University, Japan; *C. Colliex,* Universite Paris-Sud, France

We report on cross-linked carbon nitride nano-onions forming thin solid films by reactive unbalanced magnetron sputtering of graphite in an argon-nitrogen discharge. The onion shells, which contain up to 20 at% N, nucleate and grow atom-by-atom on substrates at temperatures as low as 200 °C. Nanoindentation studies reveals a highly resilient material that is relevant for wear-protective applications. Total energy calculations show the relative stability of C@sub 60-2n@N@sub 2n@ aza-fullerenes and suggests the existence of a novel C@sub 48@N@sub 12@ molecule with the unusual S@sub 6@ point group.

Vacuum Science & Technology
Room 125 - Session VST-MoA

Dry, Cryo & Other Forms of Pumping

Moderator: J.L. Provo, Sandia National Laboratories

2:00pm **VST-MoA1 Towards the Single Pump Solution - A Recent Advance in High Speed Machines for Dry Vacuum Pumping**, *A.D. Chew, P. Birch, N. Schofield, I. Stones,* ***R.G. Livesey,*** BOC Edwards, UK **INVITED**

The goal of a single (dry) pump capable of reaching high vacuum and itself exhausting to atmospheric pressure has long existed in the vacuum field. The recent development of a single shaft high speed pump mechanism has gone some considerable way to achieving this goal. The pump exploits molecular drag and fluid dynamic mechanisms. It will be discussed in terms of its science of operation, internal flow mechanisms and technology innovations enabling the mechanism to be produced in volume quantities. Further development and application examples will be discussed to illustrate system-simplification which the pump provides.

2:40pm **VST-MoA3 Effect on Capture Probability for a Commercial Cryopumpin Three Different Mounting Arrangements**, *S.B. Nesterov, Y.K. Vassiliev,* Moscow Power Engineering Institute, Russia; ***R.C. Longsworth,*** IGC-APD Cryogenics, Inc.

A recent Monte Carlo analysis by the authors of the capture probability of an APD Cryogenics M8 cryopump in a test dome per the AVS recommended practice showed it to be about 11 % higher than if tested in an idealized large standard dome (LSD). The same analysis showed that a pump with a uniformly porous inlet has the same capture probability in the test dome as the LSD. The analysis suggested that the geometry of the inlet louvers in the real cryopump and the different flow patterns in the two different domes results in the capture probability in the two different domes being different. Further studies have been done to analyze the flow patterns at the inlet to the M8 cryopump in a LSD and a test dome in order to obtain a more rigorous explanation of the difference. The analysis has been extended to the case where the M8 cryopump is mounted behind a typical gate valve to see if the test dome provides a more realistic standard than the present LSD.

3:00pm **VST-MoA4 Water Vapor Capture Within a Vacuum Chamber - The Technology of Meissner Cryopumping Yesterday and Today***, **D.J. Missimer**,* Retired **INVITED**

In 1955 C.R. Meissner revealed his in-chamber water vapor pumping concept, based on the early work of Dewar. Meissner employed both boiling liquid and heated gaseous nitrogen to rapidly temperature cycle a coil of tubing between cryogenic and above-ambient temperatures. Several vacuum system manufacturers incorporated advanced versions of the nitrogen cooled and heated "Meissner Coil" in their apparatus starting in the late 1960s. Although effective, it proved wasteful of nitrogen and difficult to control. Early closed loop mechanical refrigeration systems had reliability and low temperature limitations and were not widely used. Also they used a flammable refrigerant in the lower stage of a two-compressor cascade cycle. This was not always acceptable. In the mid-1980s a reliable single-compressor auto-refrigerating cascade (ARC) system with fast cycling capabilities between high and cryogenic low temperatures was developed. Its water vapor cryopumping proved more economical and operated with far lower power inputs than previous pumping methods. A mixture of Freons and an inert gas (argon or nitrogen) served as the refrigerant. The Freons were replaced in the 1990s by environmentally benign materials. Rapid temperature cycling of a cryopumping surface mounted directly within the vacuum space has proven its merits because of its high speed, reliability and energy efficiency.

3:40pm **VST-MoA6 Sputter-ion Pump Element Cathode to Reduce Noble Gas Instabilities***, **C.M. Schwie**,* Physical Electronics

Research not yet completed. Sputter-ion pumps have long been used to create reliable ultra-high vacuum environments. However, in certain applications, sputter-ion pumps have demonstrated instability when subjected to noble gas loading. The most stable method of pumping noble gases (e.g. argon) has historically been to employ combinations of titanium with tantalum in the pumping element. This paper evaluates new pumping element design approaches to enhance the Physical Electronics noble gas element. A solution to the problem of re-release (outgassing) of gases under vacuum lies mainly in the element's anode/cathode design. Various techniques were applied to aid the vacuum stability of a sputter-ion pump. These techniques involve employing cathode materials at various volumetric ratios and configurations to customize the pump to its expected operating environment. In addition to vacuum stability, pump speed, ultimate pressure, life, and manufacturability are the chief concerns. The evaluated designs also allow for customization of the pumping element (anode/cathode assembly) to the operating environment. The variation of cathode material ratios is an attempt to tailor the vacuum pump to the gas species present in the system. This will allow the vacuum user to achieve a proper balance between pumping speed and stability. This paper evaluates vacuum pump stability, speed (in accordance with ISO 3556), ultimate pressure, and life with the new cathode configurations. For more information contact: Name: Chester Schwie Job title: Mechanical Engineer Email address: cschwie@phi.com.

4:00pm **VST-MoA7 Compact Trapping Device Integrated with a Throttle-Cycle Cooler Operating with Mixed Refrigerant***, **M. Boiarski**, A. Khatri,* IGC-APD Cryogenics Inc.*; S.B. Nesterov, A. Androsov,* Moscow Power Engineering Institute, Russia

Trapping devices integrated with a throttle-cycle cooler operating with mixed refrigerant provide advantages in various applications. These devices can be efficient for water trapping at the inlet of turbo-molecular pumps and for oil trapping when used in combination with diffusion pumps. In addition, a mixed refrigerant cooler can provide predetermined temperature profiles of the trapping surface that can be used for selective trapping of desired substances. The refrigeration capacity and the power consumption of such coolers are discussed based on generalized experimental and theoretical data. Data on the refrigeration performance is presented for temperature ranges selected from 80 to 200 K for coolers operating with single-stage compressors. Experimental data is also presented for cooldown time. A rapid cooldown cooler can be designed with minor modifications of the existing low-cost coolers. Both the water pumping speed and nitrogen conductance are taken into account for the optimal design of the baffles. A comparative performance is given for the baffles of different configurations. The test particle Monte-Carlo method is used for simulation of gas flow in a high-vacuum system. A comparison of the calculated and experimental data was conducted for a water trap design consisting of parallel plates installed on the flattened cold finger. Experimental and calculated data on the nitrogen pumping speed are in good agreement. The deviation is less than 5%. This allows optimized configuration of the baffles using the software. Test data obtained for the water-trapping device integrated with turbo molecular pumps proves the performance to be reliable without a special temperature regulation system.

Applied Surface Analysis
Room 134/135 - Session AS-MoP

Student Poster Competition/Aspects of Applied Surface Analysis I Poster Session

AS-MoP1 Vesicle to Supported Bilayer Transformation Kinetics; Influence from Vesicle Size, Temperature and Surface Support, *E. Reimhult*[1], ***K. Dimitrievski****, V.P. Zhdanov, F. Höök, B. Kasemo,* Chalmers University of Technology, Sweden

Supported phospholipid bilayers (SPB) on solid surfaces are biologically functional components of high current interest, e.g., for biosensors, tissue engineering, and basic science (Sackman, Science 271:43 (1996)). We investigate how the kinetics of vesicle to bilayer transformation on SiO@sub 2@ depend on vesicle size using small Extruded Unilamellar Vesicles (EUV; diameter~30-200 nm) and Small sonicated Unilamellar Vesicles (SUV; diameter~25 nm)) and temperature (T~5 to 30°C).). The experimental results are complemented by computer modeling and MC simulations. Our results reveal weak but significant vesicle size-dependent kinetics. The rate and completeness of the vesicle-to-bilayer transformation is strongly dependent on temperature and the vesicle-to-bilayer formation on SiO@sub 2@ can under certain circumstances be completely inhibited at low temperatures. In addition, the vesicle-surface interaction was investigated for various surfaces, including oxidized Au, Pt and Ti, which all demonstrate adsorption of vesicles in an intact state independent of vesicle size and temperature. The obtained results extend our previous studies at constant vesicle size and temperature (Keller et al, Phys Rev B 61: (3) 2291 (2000)) and constitute a platform that will significantly improve the possibility to control the process on @micro@m-nm fabricated surfaces, from which more complex functional supported bio-membranes are constructed.

AS-MoP2 Thermal and Electron-beam Irradiation Effects on the Surfaces of Niobium@footnote 1@, ***Q. Ma****, R.A. Rosenberg,* Argonne National Laboratory

Superconducting radio frequency (SCRF) cavities represent the future for producing high acceleration gradients. Many problems encountered during the course of rf cavity production, such as the field emission of impurity particulate, have largely been solved, and nowadays gradients as high as 25 MV/m are readily achievable. However, new issues are emerging that limit further increases of the accelerating gradient. It has become increasingly apparent that further advances in cavity performance will be linked to scientifically understanding the nature of the surface oxide layer. Preliminary results of a study of the surfaces of Nb samples for SCRF cavities are presented. The samples were prepared by chemical etching or electro-polishing, the processes used in cavity production. The surfaces of such prepared samples are covered typically by a layer of oxides and some hydrocarbons. The study is focused on thermal effect on the surfaces of as-prepared samples and on electron-beam interaction with these surfaces. At temperatures from 200 C to 300 C, the surface oxide reduction occurs. The native Nb@sub 2@O@sub 5@ oxide reduces to Nb@sub 2@O@sub x@ (x @<=@ 1). Some niobium carbide also forms on the surfaces. As a result, the secondary electron yield (SEY) decreases dramatically. At these temperatures, oxygen migration into Nb is evidenced, for which the diffusion coefficient is estimated. It is also found that the SEYs of as-prepared samples decrease significantly under electron-beam irradiation, which can be accounted for by the electron-beam-induced changes in surface chemistry. These changes will be discussed in terms of the effect of the cross section of electron/matter interaction. @FootnoteText@ @footnote 1@ Work supported by U. S. Department of Energy, Office of Basic Energy Sciences, under contract no. W-31-109-ENG-38.

AS-MoP3 Determination of In-Depth Profiles Using Deconvolution of Angle Dependent XPS: Model Systems and Copolymer Surface Compositions, ***C.M. Mahoney***[2], State University of New York at Buffalo*; J. Elman,* Eastman Kodak*; J.A. Gardella, Jr.,* State University of New York at Buffalo

The depth information obtained by angle dependent XPS is not a direct measure of the composition as a function of depth. All atoms within the path of the probing X-ray will contribute to the signal, but the contribution of each will decrease exponentially with distance from the free surface. The spectra obtained are convoluted in a manner which will be more representative of the very surface, rather than deeper into the bulk. Here we test a numerical algorithm with defined boundary conditions based on polymer compositions. Unlike previous algorithms, this method was designed for samples with compositional gradients, as is common with many copolymer systems. Previously we have reported this method in studying copolymer surfaces including poly(amideurethane), Dimethylsiloxane-Urea-Urethane, and Poly(imidesiloxane) block copolymers. However, most of this work has described the relative compositions between various polymers. It is of interest to determine the accuracy of this algorithm in determining overlayer thicknesses and concentration depth profiles. The accuracy was determined through comparison of the calculated values to model systems based on polymer chain configurations. It has been determined that this method is accurate in the approximation of overlayer thicknesses in copolymer systems. The accuracy of this technique will be further examined through measurement of a reference material containing a thin layer (20-30Å) of poly(methylmethacrylate) (PMMA) deposited on Si containing its native oxide.

AS-MoP4 Defect Layer Detection at the Surface of Polycrystalline Cu(In,Ga)Se@sub2@ by SIMS Depth Profiling, AES, SEM and TEM, ***S.E. Asher****, F.S. Hasoon, H. Althani, K.M. Jones, C.L. Perkins, M.R. Young,* NREL

Polycrystalline thin-film solar cells based on the ternary chalcopyrite semiconductor Cu(In,Ga)Se@sub@2 (CIGS) have produced devices with the highest recorded efficiencies for any thin film technology, near 19%.At NREL, absorber films are grown using a three-stage process with co-evaporation of the elements in a Se atmosphere.@footnote 1@ The growth parameters of the final stage are important to obtaining high efficiency devices. Recently, cross-sectional SEM and TEM results have shown that certain third-stage growth conditions result in the formation of a defect layer near the surface of the absorber layer. This layer can be up to 250 nm thick depending on conditions. However, despite the change in microstructure, Auger depth profiles across this interface do not reliably show the presence of a compositional change. We have found that a simple SIMS depth profile following Na correlates well with the existence of the defect layer near the surface of the CIGS layer. We believe this is due to increased Na incorporation along the defects and grain boundaries in this layer. In this study, SIMS results are correlated with AES compositional profiles and SEM and TEM micrographs. SIMS provides a rapid means to access compositional changes occuring in the near surface region of the CIGS absorbers. @FootnoteText@ @footnote 1@A.M. Gabor, J.R. Tuttle, D.S. Albin, M.A. Contreras, and R. Noufi, Appl. Phys. Lett., 65, 198, 1994.

AS-MoP5 Charged Layer Calculation for an Effective Surface/Interface Analysis of Insulating Oxides using AES, ***S. Wannaparhun***[3], *S. Seal, V. Desai, K. Scammon, Z. Rahman,* University of Central Florida

Auger Electron Spectroscopy (AES) can provide compositional information with excellent spatial resolution. Unfortunately, charging problem has known to be a major obstacle for characterizing insulating materials. Four parameters affect the degree of charging phenomenon; (i) resistivity of materials, (ii) primary electron beam energy, (iii) total electron yield, and (iv) sample thickness. First three parameters have been paid attention for overcoming the problem, however the charging problem still exists. Herein, a proposed model to overcome the charging in all insulating materials has found to be successful in analyzing insulating materials. A negatively charged layer will present at the top surface when the insulating material is analyzed using an e-beam. The negatively charged layer thickness is a function of the e-beam energy and other material constants (such as density, average atomic number, and average atomic mass). The accumulated negative charges will dissipate to the ground when the sample thickness is equal or less than the charged layer. Hence, the sample thickness in this case is defined as an effective thickness. Both capacitor and double charged layer models are applied to calculate the effective thickness of insulating materials for Auger analysis without charging. The effective thickness is used as a criterion for sample preparation. Focused ion beam (FIB) technique is utilized to prepare a specimen with the effective thickness as predicted by the model for minimal or no charging during analysis. An oxide/oxide ceramic matrix composite; Nextel 720 fiber/ aluminum oxide for high temperature applications in gas turbine was selected for this study. A thin specimen including an interface between the fiber and the matrix is imaged and corresponding AES spectra are acquired from selected regions with no charging. The results are compared to a thicker sample, which suffered severe charging during AES analysis. The effective thickness for more than fifty solid oxides are also calculated using

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[1] **ASSD Student Poster Competition Participant**

[2] **ASSD Student Poster Competition Participant**

[3] **ASSD Student Poster Competition Participant**

our model for future AES analysis without charging and is presented in a periodic table format.

AS-MoP7 Innovative Design of a Temperature Controlled Sample Holder*, **D. Castro Alves**[1], O.M.N.D. Teodoro, A.M.C. Moutinho,* New University of Lisbon, Portugal

To study many surface phenomena, the sample temperature is a fundamental parameter. Adsorption and desorption, as well as diffusion, are examples of experiments where the temperature plays an important role. In this work, we described a sample holder adequate to work in a temperature range of 100K to 1200K with the possibility to achieve fast cooling and heating rates. The central part of the sample holder is similar to a ball bearing. The external piece was built in copper OHFC and is connected to the cold source a liquid nitrogen reservoir. The inner ring was made in molybdenum and holds the sample. Between this ring and the external piece, sapphire balls provide the proper thermal connection good thermal conductivity at low temperatures and poor cond uctivity at high temperatures. The sample may be tight and released via a bolt in the external piece. Since the perimeter of this piece is open, the bolt decreases the perimeter of the groove where the balls are fitted and subsequently the inner ring (als o open) is compressed against the sample. This provides a very good thermal contact without the need of welding, as is the case of many sample holders. In order to control the temperature, heating is provided by electron bombardment from the opposite side of the surface under study. A thermocouple is connected directly the sample and is used to measure the temperature. Control is performed by computer. Further details as well as heating and cooling rates will be presented.

AS-MoP8 TOF-SIMS and XPS Characterisation of Novel Perfluoropolyether-urethane Ionomers from Aqueous Dispersions*, **R. Canteri**, G. Speranza, M. Anderle,* ITC-IRST, Italy*; S. Turri, S. Radice,* Ausimont SpA, Italy

The introduction of perfluoropolyether (PFPE) bifunctional macromers, in polyurethane coatings@footnote 1,2@ has lead to an improvement of the durability characteristics and surface properties of the material, while maintaining the advantage of an easy application technology in a variety of environmental conditions and temperatures.@footnote 3@ In this work we present a surface characterisation by TOF-SIMS and XPS of a new series of polymer thin films containing PFPE macromers, applied in form of PolyUrethane Aqueous Dispersions (PUAD). In fact, environmental issues are forcing the development of waterborne polymer systems (dispersions or emulsions) to reduce the problems of solvent emissions in the atmosphere. The PUAD systems presented in this work can be defined as polyurethane ionomers, since self-dispersion in water is achieved by using co-monomers containing a -NR@sub3@ or a -COOH group, which can be salified with acids or bases. A number of experimental parameters like polymer molecular weight, crosslinking, average fluorine content as well as position of fluorinated segments in the macromolecular backbone, are investigated by selective syntheses and molecular characterization of a series of model PFPE containing polyurethane ionomers. The analysis of the outermost layer of the dried waterborne coatings by TOF-SIMS is compared with analyses by XPS obtained at two different take off angles for sampling different thickness. These results are finally compared with those obtained on the solventborne crosslinked coatings@footnote 4@ containing similar PFPE macromers. @FootnoteText@ @footnote 1@ G.Simeone, S.Turri, M.Scicchitano, C.Tonelli, Angew. Makromol. Chem. 236 (1996) 111. @footnote 2@ S.Turri, M.Scicchitano, G.Simeone, C.Tonelli, Progr. Org. Coat. 32 (1997) 205 @footnote 3@ J.Scheirs, S.Burks, A.Locaspi, Trends Polym. Sci. 3 (1995) 74 @footnote 4@ S.Turri, S.Radice, R.Canteri, G.Speranza and M.Anderle, Surface and Interface Analysis 29 (2000) 873.

AS-MoP9 Experimental vs. Theoretical Studies of Amine Reaction Pathways on Si(100)*, **A.J. Carman**[2], S.M. Casey,* University of Nevada, Reno

Theoretical analysis of methylamine (MA) and dimethylamine (DMA) adsorption on silicon clusters has been undertaken to deduce the mechanism by which small carbon- and nitrogen-containing molecules react with the silicon surface. Possible dissociative adsorption pathways have been examined including calculating transition states from the physisorbed state to the dissociated, chemisorbed products. Three reaction pathways were examined: N-H bond cleavage, N-C bond cleavage, and C-H bond cleavage, followed by adsorption of the resulting fragments. The N-H bond cleavage pathway presents the lowest transition state to dissociative adsorption for both molecules. MA adsorption on the Si(100)-(2x1) surface has also been studied experimentally using Auger electron spectroscopy (AES), low-energy electron diffraction, and thermal desorption spectroscopy (TDS). Experimental evidence shows that at room temperature MA chemisorbs dissociatively on this surface. TDS data show that the chemisorbed adsorbates can decompose via reactions that form gaseous hydrogen, ammonia, and methylimine products. AES results show that MA surface decomposition leads to the slow deposition of carbon- and nitrogen-based films. An analysis of the AES and TDS data will be discussed along with results from the theoretical adsorption studies to examine the predictive power of these computational methods.

AS-MoP10 TOF-SIMS and Laser-SNMS Characterization of Cell Cultures and Tissue Material*, **M. Fartmann**, S. Dambach,* Universität Münster, Germany*; A. Wittig, W. Sauerwein,* Universitätsklinikum Essen, Germany*; H.P. Wiesmann,* Klinik und Poliklinik für Mund-, Kiefer- und Gesichtschirurgie Münster, Germany*; H.F. Arlinghaus,* Universität Münster, Germany

In medical and pharmaceutical research, knowledge of the distribution of drugs and intrinsic elements and molecules in tissue sections and even inside individual cells is of great interest. We have applied TOF-SIMS and Laser-SNMS for imaging and quantifying atomic and molecular species in biological samples. Both techniques can simultaneously detect all masses with very high sensitivity and sub-cellular resolution. Since most of the sputtered particles are neutrals, Laser-SNMS has the additional advantage of significantly reducing the matrix effect. To prepare cell cultures for mass-spectrometric analysis, a freeze-fracturing method was used. Hereby the cells are sandwiched between two substrates before being frozen. This sandwich is then pried apart in its frozen state, so that some cells are torn. Subsequently, the samples are freeze-dried. The fractured cells can then be examined with TOF-SIMS and Laser-SNMS. Successful sample preparation is characterized by the distribution of the Na/K ratio. We have used TOF-SIMS and Laser-SNMS to examine freeze-fractured, freeze-dried bone and cancer cell cultures and freeze-dried cryosections of bone tissue. For analysis, a gridless reflectron-type TOF mass spectrometer with a 30 keV Ga LMIG and an excimer laser was used. For nonresonant postionization, the excimer laser beam (wavelength = 193 nm) was focused down in front of the target. With both techniques, high resolution elemental and molecular images and mass spectra were obtained from cell cultures and tissue samples. Ion-induced electron images were obtained to identify individual cells. The measurement of the Na/K ratio clearly showed that the preparation technique preserves the chemical und structural integrity of the cells. It can be concluded that TOF-SIMS and Laser-SNMS are well suited for imaging trace element and molecule concentrations in biological tissues.

AS-MoP12 Evaluation of the Surface Morphology of Chemically Treated Fluorides by AFM*, **M. Suzuki**,* Tohoku Institute of Technology, Japan

Alkaline earth fluorides are suitable materials as substrates for the epitaxial growth of several semiconductors, and the (111)surface of cleaved CaF@sub2@ or BaF@sub2@ and (Ca,Ba)F@sub2@ buffer layers on (111)Si have mainly been used. The crystalline quality of epitaxial layers are influenced by the surface morphology and structure of fluoride substrates and it has been known that bombardment of energetic electrons or ultra-violet irradiation makes the surface structure of fluorides change and improve the quality of epitaxial layers on them. In this study, wet chemical treatments were applied to fluoride substrates and their effectiveness was evaluated in improving the surface morphology by atomic force microscopy(AFM) and reflection high energy electron diffraction(RHEED). The polished (111)CaF@sub2@ and BaF@sub2@ substrates with optical flatness were chemically treated at room temperature by using diluted solutions of HF,HCl, and NH@sub4@Cl for the different concentrations and treatment times . The morphological changes of substrates by treatment with different solutions were compared in detail. The best results were obtained for the CaF@sub2@ treated with 16.3%HF for 15 minutes and for the BaF@sub2@ with 0.3%HCl for 35 seconds. Under this condition, the surface roughness(rms) of both substrates could be obtained to be within a few nanometers, which provides a capability for epitaxial growth of high quality layers . Evaluations with RHEED would be also discussed.

AS-MoP13 Impurity Dopant Profile Measurement and Quantization in sub-100nm Region*, **E.-S. Kang**, H.-J. Hwang,* Chung-Ang University, Korea*; G.-Y. Lee,* Samchok National University, Korea

We have quantitatively extracted 1-dimensional carrier profiles from the scanning capacitance microscope (SCM) dC/dV versus V curves using the SCM inversion modeling. This is based on the spherical capacitor model not the common parallel-plate capacitor model. Since the current SCM system has a poor reproducibility for obtaining the local dC/dV curves in the higher

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dopant concentration region, this problem will prevent us from acquiring carrier depth information correctly. For the more accurate inverted dopant profile in sub-100nm region, therefore, we have added some factors such as SCM tip/sample interaction and fully-calculated volume charges into previous modeling parameters. Also, we have designed a new capacitance detector operating about 1.8GHz frequency. It consists of a voltage-controlled oscillator with PLL (Phased-Lock Loop), a microstrip resonator, a RF mixer IC for detecting the capacitance variations. This technique will bring a greater enhancement for the current SCM sensitivity and performance.

AS-MoP14 Non-destructive Testing of Mechanical Properties of Thin Films below 100 nm with Laser-acoustic Waves*, T. Schuelke,* ***D. Schneider****, B. Schultrich,* Fraunhofer Institute for Materials and Beam Technology

The non-destructive testing of hard-coatings is highly desirable. The available test methods are permanently confronted with manifold new demands of the surface engineering arising from reducing film thickness, more complicated film composition and extreme mechanical requirements as high hardness, stiffness and adhesion. The laser-acoustic technique based on surface acoustic waves is a relatively new surface test method, but its capability for testing thin and hard coatings has already been demonstrated. The laser-acoustic method yields the Young's modulus revealing the effect of varying bonding structure of the material, porosity and other micro-defects, including insufficient adhesion. The method has been adapted to the requirements of testing ultra-thin films. The special methodical aspects of testing these films are presented, such as the effect of measuring accuracy, bandwidth and sample dimension.

AS-MoP15 Atomic-Scale Modeling of Plasma Enhanced Chemical Vapor Deposition of Hydrogenated Amorphous Silicon Thin Films*, S. Sriraman*[1]*,* ***S. Ramalingam****, E.S. Aydil, D. Maroudas,* University of California, Santa Barbara

Hydrogenated amorphous silicon (a-Si:H) thin films grown by plasma assisted deposition from silane containing discharges are widely used in photovoltaic and flat-panel display technologies. Despite extensive research, the elementary processes that lead to film deposition, H incorporation, and defect generation are still not well understood. Developing deposition strategies for improving film quality requires a fundamental understanding of the interactions of radicals, such as SiH@sub x@ (0<x<4) and H, with the deposition surface. Using a hierarchy of atomistic simulation tools based on molecular-dynamics (MD), molecular-statics, and Monte Carlo methods, we have studied the growth of a-Si:H on H-terminated Si(001)-(2x1) surfaces through MD simulations of repeated impingement of SiH@sub 3@, SiH@sub 2@ and SiH radicals, separately, as precursors. Special emphasis was placed on the identification of the elementary surface chemical reactions that govern the deposition process. The effects of reactions on the growth surface are examined by analyzing local structural configurations and surface chemical reactivity in the vicinity of the surface reaction sites. The evolution of the films' structure, surface morphology and roughness, surface reactivity, and surface composition are analyzed in detail, and comparisons made between the films deposited from individual SiH@sub 3@, SiH@sub 2@ and SiH precursors. Experimental measurements of the surface silicon hydride composition and results from atomistic simulations will be synergistically used to elucidate elementary processes occurring on the surface and discuss our current understanding of the a-Si:H deposition process.

Biomaterials

Room 134/135 - Session BI-MoP

Biorecognition Poster Session

BI-MoP1 Silica-Elastin Like Polypeptide Smart Membranes-Switchable Molecular Filters*,* ***G.V. Rama Rao****, S. Balamurugan, G.P. Lopez,* The University of New Mexico*; D. Meyer, A. Chilkoti,* Duke University

Elastin-like polypetides (ELPs) are a class of synthetic polypetides comprising of Val-Pro-Gly-Xaa-Gly where Xaa is any amino acid with the exception of proline and exhibit inverse solubility temperature behavior in aqueous solutions. They undergo a transition from hydrophilic (extended conformation) to hydrophobic (compacted conformation) at the lower critical solution temperature (LCST). We demonstrate in this study that when ELPs are encapsulated in a silica matrix, the ELPs can act as molecular switches that control the selective permeability of the membranes. The pores resulting from the transition can selectively transport different molecular species depending on their size. Two different ELPs of molecular weights of 60 kDa (ELP1-150) and 13 kDa (ELP4-30) were used for the present study. Silica-ELP membranes were prepared by sol-gel processing on microcon centrifugal filter units with 30,000 -100,000 molecular weight cut-off membranes and on 1 inch diameter of ultrafiltration discs. The LCST of the membranes was established by permeation measurements and static contact angle measurements. Differential scanning calorimetric studies were employed to determine the LCST of bulk gels and found to be 34 and 44°C for ELP1-150 and ELP4-30 respectively. Cycling of the membranes between 25 and 40-45°C indicates that the membranes possessed reversible, variable permeability while maintaining good mechanical stability. Permeation experiments with various molecular weights of poly(ethylene glycol) (PEGs) on centrifugal filters and ultrafiltration membranes clearly demonstrated that these membranes are acting as a molecular switches by being impermeable below the LCST and permeating the lower molecular weights of PEGs and filtering out higher molecular weight PEGs above LCST.

BI-MoP3 The Silanisation of Tantalum Pentoxide for Biosensor Realisation*,* ***W. Laureyn****, F. Frederix, A. Campitelli,* IMEC, Belgium*; J.-J. Pireaux,* FUNDP, LISE, Belgium*; G. Maes,* KULeuven, Belgium

Affinity biosensors allow the detection of affinity based interactions between bio-molecules, which occur e.g. in antibody-antigen recognition or DNA hybridisation. The presence of antigens in an analyte can be verified by the binding of these molecules to their complementary antibodies, immobilised onto a biosensor surface. Tantalum pentoxide is considered as a material with unique properties for biosensor realisation, being chemically very stable and attractive from an electronic point of view, owing to its high dielectric constant. In order to realise tailored bio-interfaces; bromoalkyltrichlorosilanes were deposited on Ta@sub2@O@sub5@. The use of chlorosilanes (as opposed to alkylethoxysilane derivatives) leads to the formation of reproducible and close-packed monolayers on the oxide surface. To allow antibody binding, the bromo-functionality was converted into a carboxyl-functionality, via a one step reaction with mercaptoacetic acid. XPS, FT-IR, contact angle goniometry, cyclic voltammetry and impedance measurements were applied for the characterisation of the cleaning of Ta@sub2@O@sub5@, its silanisation and of the demanded surface reaction. The results of this study indicate the success of our approach. Moreover, distinct differences are revealed for (mixed) silane monolayer formation with short or long-chain chlorosilanes, from the liquid or vapour phase. In future work, the use of bromoalkyltrichlorosilanes will be compared to the silanisation of Ta@sub2@O@sub5@ with allylalkyltrichlorosilanes, followed by an oxidation in order to generate carboxyl groups. This procedure will also allow the immobilisation of antibodies on Ta@sub2@O@sub5@.

BI-MoP4 Organization of Multifunctional Co-polymers on Metal Oxide Surfaces for Optical Biosensing Applications*, N.-P. Huang,* ***I. Reviakine****, S.M. De Paul, M. Textor, N.D. Spencer,* ETH Zürich, Switzerland

A novel polymeric interface that combines the resistance to non-specific protein adsorption conferred to metal oxide surfaces by poly(L-lysine)-g-poly(ethylene glycol) (PLL-g-PEG) with the high affinity of the well-known (strept)avidin-biotin system through the use of a biotinylated-PEG-containing copolymer (PLL-g-PEG/PEGbiotin) has recently been introduced by our group for use in biosensing applications. Biosensor chips with high sensitivity and selectivity can be designed with the above approach, making it an attractive surface technology. Optimization of this system for various biosensor applications depends critically on the knowledge of how the polymer film is organized at the metal oxide interface. Therefore, this work focuses on investigating the organization of the co-polymer film by atomic force microscopy (AFM), quartz crystal microbalance with dissipation (QCM-D) and optical waveguide lightmode spectroscopy (OWLS). This combination of spectroscopic and imaging techniques provides an insight into how the co-polymer mixture is organized at the surface and how this organization evolves with time. The effect of streptavidin addition was also investigated and biotinylated liposomes were used as a well-understood model analyte in AFM and QCM studies.

BI-MoP5 Investigation of the Immobilization Process of Peptide Nucleic Acids*,* ***J.C. Feldner****, M. Ostrop, O. Friedrichs, G. Gappa, D. Lipinsky, U. Gunst, S. Sohn, H.F. Arlinghaus,* Universität Münster, Germany

In order to immobilize peptide nucleic acid (PNA) onto Au and Ag coated surfaces, a thiol linker (DTSP, 3,3'-Dithio-bis(propionic acid N-hydroxysuccinimide ester)) was used. The immobilization process of DTSP

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[1] **ASSD Student Poster Competition Participant**

and PNA to these surfaces can be performed by either binding PNA to DTSP in a solution and then immobilizing it onto the surface or immobilizing DTSP onto the surface and then attaching PNA to it. In both methods, PNA binds to the reactive end group of DTSP and the thiol group of DTSP binds to the Au or Ag surface. The reactive end groups of the DTSP layer can be inactivated using primary amines after immobilization of PNA. Deprotenated (M-H)@super-@ signals of the different PNA bases as well as characteristic peaks of DTSP fragments could be used in TOF-SIMS and TP-SIMS (temperature programmed SIMS) measurements to study and optimize the different immobilization processes. A detailed investigation of the concentration of DTSP and its immobilization time on Au and Ag surfaces showed that the best result could be achieved at a concentration of 10 mM and an immobilization time of 24 hr. The binding of PNA to the DTSP layer takes significantly longer than attaching DTSP to the surface. TP-SIMS data, which are very sensitive to bonding strength, showed that characteristic ion signals of the bases start to decrease at a temperature of about 150°C, with differences in the point of onset for the different bases. From the obtained data it can be concluded that the second attachment method described above is preferable to the first one and also has the advantage of allowing to inactivate the complete Au or Ag surface for unspecific DNA attachment.

BI-MoP6 Biotin-reactive Surfaces Based on @OMEGA@-substituted Alkanethiols on Au(111), ***H. Tran**, M. Chen, H. Lu, A. Neurauter, S. McManus-Munoz, D. Quincy, T. Langenbacher, P. Peluso, P. Kernen, S. Nock, P. Wagner,* Zyomyx, Inc.

(Oligo)ethylene glycol-containing alkanethiols with @omega@-substituted N-hydroxysuccinimide-ester groups self-assemble in ordered monolayers on Au(111) surfaces (NHS-SAM) and form highly reproducible reactive interfaces for in-situ transformations and biomolecular immobilization. Surface sensitive spectroscopic techniques including FTIRRAS, and XPS, indicate that amino-biotin can be successfully coupled in-situ to the NHS-SAM. Such reactive surfaces have been tested for homogeneous surface coverage and selective binding of streptavidin- and biotin-conjugated dyes and proteins using fluorimetry, radiometry and surface plasmon resonance. These binding data on biotin-functionalized SAMs are compared with binding efficiencies of electrostatically adsorbed biotin derivatized poly(L-lysine)-grafted poly(ethylene glycol) layers on Au(111) surfaces. We incorporated these bioreactive interfaces into microfabricated three-dimensional structures in silicon and used these to test an immunoassay in a microarray format.

BI-MoP7 Reactivities and Biomolecular Immobilization on Self-assembled Alkanethiols with @OMEGA@-substituted N-hydroxysuccinimide-ester Groups on Au(111), ***S. McManus-Munoz**, D. Martin, C.E.J. Dentinger, R.L. Cicero, H. Tran, M. Chen, P. Kernen, P. Wagner,* Zyomyx, Inc.

Alkanethiols with @omega@-substituted N-hydroxysuccinimide ester groups have been self-assembled on Au(111) surfaces. Stability and reactivity of the functional group were studied using reflection absorption infrared spectroscopy, contact angle, ellipsometry and radiometry measurements. Increased NHS-reactivity was observed for alkanethiols containing (oligo)ethylene glycol units. Effective NHS quenching combined with some effects on non-specific protein adsorption was found with various amino-containing compounds, e.g. glycine and amino-PEGs. Transformation of the NHS-group into a biotin exposing surface was obtained by in-situ coupling of amino-biotin. Specificity and homogeneity of streptavidin and biotin-conjugated protein binding was tested by spectroscopic and microscopic techniques and compared with the binding efficiencies on physisorbed polymer layers of biotin derivatized poly(L-lysine)-grafted poly(ethylene glycol) on metal oxides and on Au(111).

BI-MoP8 Measuring Bound Water in Protein-resistant Coatings: A Combined OWLS and QCM-D Study of Poly(L-lysine)-g-poly(ethylene glycol), ***S.M. De Paul**, J. Vörös, I. Reviakine,* ETH Zürich, Switzerland; *C. Galli, M. Collaud Coen,* University of Fribourg, Switzerland; *M. Textor, N.D. Spencer,* ETH Zürich, Switzerland

Metal oxide surfaces coated with poly(L-lysine)-g-poly(ethylene glycol) (PLL-g-PEG) have been shown to resist non-specific adsorption of proteins. The hydrophilicity of the PEG chains is believed to play a crucial role in such behavior. In order to determine the amount of water coupled to PLL-g-PEG at aqueous metal oxide interfaces, we use results from two in situ methods: optical waveguide lightmode spectroscopy (OWLS), which detects the mass of polymer adsorbed at the surface, and quartz crystal microbalance with dissipation (QCM-D), which is sensitive to the mass of the polymer plus the mass of trapped or hydrodynamically coupled water. Complementary information about water content is provided by solid-state NMR measurements. We also examine how the amount of adsorbed polymer and its protein resistance vary with the choice of substrate (e.g., TiO@sub 2@, SiO@sub 2@) and with the surface topography as determined by atomic force microscopy (AFM).

BI-MoP9 Examination of Bacterial and Protein Attachment and Release Using Tunable Poly(N-Isopropylacrylamide) as a Switchable Hydrophobic/Hydrophilic Substratum, ***L.K. Ista**, S. Mendez, S. Balamurugan, G.P. Lopez,* The University of New Mexico

Poly(N-isopropylacrylamide), or PNIPAAM, undergoes a critical solubility transition in response to temperature. Below 32°C, the polymer is freely water soluble, whereas above this temperature it is insoluble in water. When PNIPAAM is immobilized this property translates to an increase in surface hydrophobicity above the transition temperature (T@sub t@). The process is fully reversible, with restoration of the original degree of solubility or hydrophilicity occurring upon cooling to temperatures below T@sub t@. This switchable characteristic of grafted PNIPAAM has been exploited in the creation of fouling release surfaces. It has been discovered that when thin layers of PNIPAAM are grown from initiator-derivatized. alkanethiolate self-assembled monolayers (SAMs), the range of wettabilities observed above and below T@sub t@ can be tuned by altering the hydrophobicity of the underlying SAM. Because the hydrophobic/hydrophilic transition happens in situ, and rapidly over a short temperature range, tunable PNIPAAM substrata are ideal for examining the effect of changing surface hydrophobicity on the attachment and detachment of biofilm components, i.e. microbes and proteins. We report here the results of attachment and detachment studies on patterned tunable PNIPAAM surfaces using two bacteria which normally exhibit different and opposite responses to subtratum hydrophobicity (Halomonas marina and Staphylococcus epidermidis) as well as studies on adsorption and desorption of a variety of proteins known to play a role in biofilm formation.

BI-MoP10 Novel Immunosensor Interfaces Based on Mixed Self-assembled Monolayers of Thiols, ***F. Frederix**, W. Laureyn, K. Bonroy,* IMEC, Belgium; *W. Dehaen, G. Maes,* KULeuven, Belgium

An ideal biosensor is characterized by its stability, reproducibility sensitivity and specificity towards a desired analyt. However, reduction of the size of the transducer and thus of the active area, requires an optimization of the sensing area. Our research is therefore also focussing on the biological recognition layer, which is based on an optimized covalent coupling of the antibodies to mixed self-assembled monolayers of thiols on gold. Since cleanliness and structural properties of the gold are of the utmost importance for perfect SAM formation, we have evaluated different cleaning procedures and induced the gold(111) structure. Characterization was performed with XRD and STM. The stability of the SAMs on gold with various properties was evaluated. To attach antibodies and/or avoid non-specific adsorption, novel thiols were synthesized. For standard covalent coupling procedures mercaptoethanol and ethanolamine are normally used as blocking molecules. We have synthesized blocking molecules based on ethylene oxide groups which show enhanced properties towards non-specific adsorption. The mixed monolayer formation was characterized using contact angle, cyclic voltammetry, impedance spectroscopy, XPS and GA-FTIR. The advantages of an orientated immobilization of chemically modified antibodies are demonstrated using SPR. We have evaluated the random amino and streptavidine-biotin coupling in comparison with the orientated aldehyde and thiol coupling procedures. Also the chemical modifications of these antibodies were optimized towards an increased sensitivity. Finally, we compared the sensitivity and selectivity with commercially available biological recognition layers, illustrating their enormous potential for further sensing applications.

BI-MoP11 Piezoresistive Microcantilever Sensors for the Detection of Biological Molecules, ***T.L. Porter**, M.P. Eastman, D.L. Pace, T.R. Dillingham,* Northern Arizona University

Microsensors capable of recognizing single biological molecules have been fabricated using piezoresistive microcantilever technology. Using 25 base single strand DNA layers as the active sensing material, small piezoresistive microcantilevers in contact with this surface were able to recognize the presence of the complimentary strand, while ingoring the presence of strands differing by 2-5 base units. The analyte recognition is by means of a simple resistance change in the microcantilever, meaning only simple, inexpensive electronics are required for this device. Several sensors may be grouped together to form small bio-sensing arrays.

BI-MoP12 Protein Template-Imprinting to Enhance Specific Protein Adsorption and Cell Adhesion*, **J. Wang**, X.H. Cheng, J. Schwartz, B.D. Ratner,* University of Washington

Molecularly imprinted polymers (MIPs) are synthetic materials that possess specific recognition properties, and have found applications in enantiomer separation, enzyme mimics, and biomimetic biosensors. Among the common methods for molecular imprinting, the self-assembly approach is important for its resemblance to antibody-antigen, substrate-receptor, and enzyme-inhibitor interactions.@footnote 1@ The key for MIPs to perform recognition is that both the template and imprint are complementary in size, shape, and chemical functionality at the binding site. Nevertheless the self-assembly approach to molecular imprinting has been primarily done in organic solutions, and is less successful in directly imprinting larger biomolecules (proteins). Shi et al.@footnote 2@ developed an alternative approach to imprint protein molecules with disaccharide molecules and polymeric thin films. The protein imprints can preferentially recognize the original template protein, which is mainly attributed to cooperative non-covalent interactions including hydrogen bonds, hydrophobic interactions and van der Waals forces. We applied a similar imprint process with optimized conditions to create highly reproducible albumin (Alb) and fibronectin (FN) imprint surfaces. Surface analyses including ESCA, SIMS, and AFM were performed to characterize the variation in chemical composition after each imprint step. BAE cell adhesion studies demonstrated that the FN imprint surface could enhance cell attachment. Results from @super 125@I labeled binary protein competitive adsorption also showed that the FN imprint surface could preferentially adsorb higher amount of FN in a binary protein solution with Alb as the competing protein. @FootnoteText@ @footnote 1@Haupt, K. and Mosbach, K. Trends Biotechnol. (1998) 16: 468-475 @footnote 2@Shi, H., Tsai, W., Garrison, M., Ferrari, S. and Ratner, BD.. Nature. (1999) 398: 593-597.

BI-MoP13 Surface Technologies to Optimize Osteopontin-immobilized Surfaces for Healing Biomaterials*, S.M. Martin,* University of Washington*; **R. Ganapathy**,* University of Washington, U.S.A*; T. Kim,* University of Washington*; L.A. Martinson,* University of Washington, U.S.A*; D. Leach-Scampavia, S.L. Golledge, C. Giachelli, B.D. Ratner,* University of Washington

Our efforts to develop biomaterial surfaces that modulate the healing and inflammatory response focus on immobilizing specific biological triggers of healing onto a bland, relatively non-protein adsorptive surface. This study illustrates the use of surface analysis tools to characterize such surfaces. Osteopontin (OPN) is a protein known to regulate inflammatory responses. Although its precise role is not fully understood, it has been implicated in wound-healing processes. We have thus chosen OPN as the protein to immobilize in these model experiments. ESCA data in our laboratory demonstrated that poly(2-hydroxyethyl methacrylate) (pHEMA) shows low protein adsorption, making it a suitable material for our immobilization studies. In the present study, a technique using carbonyldiimidazole (CDI) was used to immobilize OPN to the polyHEMA surface. We employed several techniques to verify presence of protein on the polyHEMA surface (ESCA, TOF-SIMS, FTIR) and quantified the amount immobilized (ELISA, radioiodination of OPN). ESCA high-resolution N 1s spectra indicated existence of OPN on the surface, and this data was confirmed by TOF-SIMS. Furthermore, data using I-125-labeled OPN showed a dose-response corresponding to the varying amounts of OPN used for the immobilization experiment. Though less accurate than the radiolabel data, the ELISA showed protein amounts in a similar range as well. These findings represent an important first step toward the creation of novel healing materials for biomedical applications and to using modern surface analytical tools to verify the surface engineering of a biomaterial. Studies funded by UWEB, EEC9529161.

BI-MoP14 Competitive Oligonucleotide Adsorption Equilibria at a Silane-Water Interface*, **A.D. Suseno**, R.S. Gascon, J.L. DelosReyes, J.E. Forman,* Zyomyx, Inc.

Adsorption of complimentary oligonucleotide sequences to surface bound oligonucleotide probes can produce surface bound duplex structures that are more prone to dissociation than their solution phase counterparts. The stability (as indicated by the observed melting temperature or Tm) can be altered by a number of factors, including probe orientation on the surface and surface bound probe density. A bound orientation that does not allow the probe to fully interact with its complimentary sequence can result in a non-optimal (and thus lower stability) duplex structure. Such effects are expected when immobilized probes are bound through exo-cyclic amines or crosslinking of thymidine residues to the surface. For surface bound probe densities, crowded surfaces that limit the amount of bound target through unfavorable steric and/or electrostatic interactions serve to destabilize the surface bound duplexes. Likewise, surfaces that interact with the immobilized probe, will compete with adsorption of complimentary sequences and can ultimately reduce duplex stability. Yet, despite these potential hindrances to duplex formation, surface bound probes can adsorb complimentary sequences from solutions in which those sequences are present in double stranded form (where the second strand is non-complimentary to the surface bound probes). We will present results from experiments in which covalently immobilized oligonucleotide probes on silanated substrates interact with both single- and double-stranded oligonucleotide target sequences to illustrate consequences of surface immobilization strategy, as well as what effect the introduction of a competing solution phase duplex formation equilibria has on adsortion to the surface bound probes.

Dielectrics

Room 134/135 - Session DI1-MoP

High K Dielectrics Poster Session

DI1-MoP1 Generation and Relaxation of Positive Charge in Gate Dielectric of MOS Structures at High-fields*, **G.G. Bondarenko**,* Moscow Institute of Electronics and Mathematics, Russia*; V.V. Andreev, A.A. Stolyarov,* Bauman Moscow State Technical University, Russia

In this work the new technique of investigation of generation and relaxation processes in gate dielectric of MOS structures during and after high-field stress is proposed. The technique is based on the controlling of current stress, applied to the sample, and simultaneous voltage measurement on it. The technique proposed allows carrying out the controlled electron injection into gate dielectric at high-fields, realizing the simultaneous monitoring of MOS structures charge state change both under the present field and under lower fields, that gives possibility to obtain new quality information about charge generation processes in dielectric layers. The technique allows, right after high-field injection without sample re-switching, to monitor the relaxation processes of charges generated by injected electrons in gate dielectric of MOS structures in wide range of electric fields, from the injection field to the structure short circuit. Using the technique proposed the investigation of positive charge generation and relaxation phenomena in silicon MOS structures with thermal SiO@sub 2@ film had been carried out. It was shown that under high injection current densities, the positive charge value monitoring by voltage shift on MOS structure can lead to significant error, to decrease which it is necessary to measure the positive charge value using voltage shift under less current densities. It was found out that the relaxation time of positive charge, generated by tunnel Fowler-Nordheim electron injection from silicon in thermal SiO@sub 2@ film, has field dependence, decreasing with external electric field rise.

DI1-MoP2 Stability of Chemical Vapor Deposited Thin Films HFO@sub 2@ and HFSi@sub x@O@sub y@*, **H. Bhandari**, V. Rangarajan, T.M. Klein,* University of Alabama

Two desirable properties for candidate high dielectric constant materials for MOSFET gates are that the material remains amorphous and does not react with silicon substrate during post deposition anneals. Uncontrolled multiple oxide layer growth during post deposition anneals can result in a decrease in the overall capacitance while a polycrystalline or phase-separated material could have excessive current leakage along grain boundaries. Hafnium oxide and hafnium silicate are two materials, which are predicted to be thermodynamically stable with silicon at 1000°C. We have deposited these materials using organometallic chemical vapor deposition with Hf (IV) t-butoxide and various oxygen atom sources including N@sub 2@O and O@sub 2@, as well as remote N@sub 2@O and O@sub 2@ plasmas. Rapid thermal annealing experiments were performed in Ar, O@sub 2@ and N@sub 2@ ambients up to 1000°C. Thin film stability was examined using XPS, Fourier transfer infrared spectroscopy and X-ray diffraction measurements.

DI1-MoP3 A Study of MOS Characteristics of Reoxidized HfO@sub 2@ Thin Film for Gate Oxide Applications*, **H.-J. Choi**, D.W. Lee, J.-H. Yoo, S.-W. Nam, D.-H. Ko,* Yonsei University, Korea*; J.-H. Ku,* R&D Center Semiconductor Samsung Electronics Co.*; M.-H. Cho,* Yonsei University, Korea*; S. Choi,* R&D Center Semiconductor Samsung Electronics Co.*; C.-W. Yang,* Sungkyunkwan University, Korea

We investigated the change of the microstructure which depend on the thickness of Hf films deposited by DC magnetron sputtering on Si substrate for gate dielectric application. Also, we estimated the electrical property and the microstructure of the interlayer between the thin HfO@sub 2@ films and Pt and Al gate electrode. The Hf films reoxidized by the RTP(rapid thermal processing) were analyzed by spectroscopic ellipsometry, AFM, XRD, XPS, and HR-TEM. We observed small grains of the HfO@sub 2@ film due to the local crystallization of the as-deposited Hf film ~90Å by HR-TEM. The thickness of the interfacial layer between hafnium oxide and Si substrate was about 8Å. After RTP treatment at 800°C in N@sub 2@ ambient, the thickness of interfacial layer was equal to that of as-deposited film. For 500Å thick as-deposited Hf film, the HfO@sub 2@ layer at the surface was observed about 55Å by HR-TEM. The HfO@sub 2@ layer increased to be 90Å at 800°C in N@sub 2@ ambient. Especially, the HfO@sub 2@ grains were shown not only at the surface of the Hf film but also at the silicide(Hf@sub 5@Si@sub 4@) grain boundaries. And the buckling of the silicide film on the Si substrate was locally observed due to the stress generated during the silicide and hafnium dioxide formation. XRD peaks indicated the formation of silicide after RTP treatment over 700°C. We evaluated C-V and I-V of the MOSCAP structures in the Pt/Hf(~100Å)/Si and Al/Hf(~100Å)/Si , and it demonstrated that the capacitance and the leakage current level of the MOS structures were changed upon the temperature of RTP treatments.

DI1-MoP4 Investigation of Tungsten Silicide Gate for the Integration with High-k Hafnium Oxide (HfO@sub 2@) in Metal-Oxide-Semiconductor Devices*, **K. Roh**, S. Yang, H. Kang, Y. Roh, G. Bae, D. Jung, N.-E. Lee, C.-W. Yang,* Sungkyunkwan University, Korea

Sub-0.1 µm MOSFETs face a scaling limit when a SiO@sub 2@ gate dielectric is used due to high direct tunneling leakage current. Recently, many high-k gate dielectrics such as Al@sub 2@O@sub 3@, Y@sub 2@O@sub 3@, ZrO@sub 2@, HfO@sub 2@ and their stacks have been studied extensively to replace thermal SiO@sub 2@. Among those dielectrics, Hafnium oxide and their silicates have been suggested as a strong candidate for the alternate gate oxides. In this work, we report the structural and electrical properties of HfO@sub 2@ films with tungsten silicide (WSi@sub 2@) as a metal gate. The samples were fabricated on 4-in n- and p-type (100) wafers with 4~7 @ohm@cm resistivity. Hf films were deposited using rf reactive magnetron sputtering method from 99.5 % Hf target on the Si wafers, and were thermally oxidized in furnace at 500 °C. Annealing of the formed HfO@sub 2@ in furnace at 500 °C was then followed. During sputtering, the gas pressure and rf power were 10 mTorr and 50 W, respectively. Tungsten silicide films for gate electrode were deposited directly on the HfO@sub 2@ films in a cold-wall low pressure chemical vapor deposition system with the thickness of 500 ~ 1500 Å. For electrical characterization, the WSi@sub 2@/HfO@sub 2@/Si MOS capacitors were. Additional annealing was carried out at various conditions to minimize the resistance of WSi@sub 2@ and etching damage. The hysteresis of the WSi@sub 2@/HfO@sub 2@/Si MOS capacitors before and after annealing was negligible (<10 mV); it was independent on frequencies from 10 kHz to 1 MHz and on bias ramp rates from 10 mV to 1 V. Gate depletion effect was not also observed. After furnace annealing of the WSi@sub 2@/HfO@sub 2@/Si MOS capacitors at 500 °C, EOT (equivalent oxide thickness) was reduced from 26 to 22 Å. In addition, the leakage current was 1x10@super -5@ A at 1 V after annealing, which is reduced by approximately one order as compared to that measured before annealing.

DI1-MoP5 Annealing Effects on Optical Properties of Hafnium Oxide Films Observed by Spectroscopic Ellipsometry*, **Y.J. Cho**, N.V. Nguyen, C.A. Richter, J.R. Ehrstein,* National Institute of Standards and Technology

We have applied spectroscopic ellipsometry (SE) to investigate a set of HfO@sub 2@ films and correlate their optical properties with fabrication processes, in particular, with high temperature annealing. Among the many proposed high-k dielectrics such as HfO@sub 2@, Ta@sub 2@O@sub 5@, TiO@sub 2@, and ZrO@sub 2@, the use of HfO@sub 2@ films as the replacement for SiO@sub 2@ as the gate dielectric in CMOS devices has received much attention recently due to its high dielectric constant, low leakage current, good thermal stability, and interface characteristics comparable to silicon dioxide/silicon interface. In spite of these promising properties, little is known about the optical properties of HfO@sub 2@. Thin HfO@sub 2@ films were grown on Si substrate by dc magnetron sputtering and then annealed at high temperatures. SE measurements were performed on a high-accuracy custom-made spectroscopic ellipsometer. The dielectric functions of these films were determined by inversions of SE data and compared with the results with those obtained by using a Tauc-Lorentz (TL) dispersion function. It will be shown that, in the near-IR-visible-UV spectral range, TL can be used to effectively describe the optical properties of HfO@sub 2@. From the characteristics found in the pseudo-dielectric functions or the TL dispersions, when the annealing temperatures increase from 500 to 700 °C, we observed that, for the HfO@sub 2@ films, the optical band gap increases. In addition, for samples annealed at 600 °C and above, new optical features, which are not present at lower temperature, are clearly seen in their dielectric functions. These features are the signature of poly-crystallization in the film attributable to the annealing. As a result, we conclude that SE can easily and quickly identify the onset or the existence of crystalline HfO@sub 2@ films without employing a more elaborate and destructive method such as a transmission-electron microscope (TEM).

DI1-MoP6 Physical and Electrical Characteristics of W-TiN/HfO@sub 2@/Si (MOS) Devices*, **S. Yang**, K. Roh, H. Kang, Y. Roh, K. Kim, N.-E. Lee,* Sungkyunkwan University, Korea

Recently, the metal/high-k oxide structures have been investigated extensively to implement sub-100 nm MOSFETs technology. In this work, we present the physical and electrical characteristics of MOS capacitors with HfO@sub 2@ gate dielectric and W/TiN gate electrode. The Hf thin films were deposited directly on n-type silicon substrate by a RF magnetron sputtering method. The HfO@sub 2@ films with thicknesses of 6-7 nm were formed by a thermal oxidation of Hf thin film in O@sub 2@ ambient at 500 °C for 120 min in furnace. The annealing of the HfO@sub 2@ films was then carried out in N@sub 2@ ambient at 500 °C for 60 min in furnace. TiN films (30 nm) were deposited on HfO@sub 2@ by a DC reactive sputtering method followed by W deposition (200 nm) using LPCVD. For some samples, only the W films were deposited on HfO@sub 2@ films to investigate the roles of the TiN films. The sheet resistance of W/TiN was ~ 4 @ohm@/square. The intermediate layer between gate dielectric and Si was observed by TEM, which is believed to be a hafnium silicate (HfSi@sub x@O@sub y@) layer. To evaluate the EOT and leakage current characteristics, the C-V and I-V measurements of MOS capacitors with different gate electrode (i.e., W/TiN, W and Pt gate) were performed. The hysteresis of W/TiN gate was negligible (100 mV) due to gate dielectric damage during sputtering deposition. The EOT of W/TiN/HfO@sub 2@ MOS capacitors was 1.9 nm based on the C-V measurement. In addition, as compared to the results obtained from the W/HfO@sub 2@/Si MOS structures, the W/TiN/HfO@sub 2@/Si MOS capacitors showed an excellent current-voltage characteristics: The leakage current was ~2x10@super -5@ A/cm@super 2@ at 2 V which is lower than published results reported by other researchers at the same EOT.

DI1-MoP7 Characteristics of HfO@sub 2@/HfSi@sub x@O@sub y@ Film as an Alternative Gate Dielectric in Metal-Oxide-Semiconductor Devices*, **H. Kang**, Y. Roh, G. Bae, D. Jung, C.-W. Yang,* Sungkyunkwan University, Korea

Recently, research efforts on high-k gate oxides have been focused on materials such as HfO@sub 2@, ZrO@sub 2@, and their silicates due to their excellent electrical properties. In particular, the HfO@sub 2@/HfSi@sub x@O@sub y@ gate-oxide produces the excellent interfacial properties between HfSi@sub x@O@sub y@ and Si, while the effective dielectric constant can be further increased by forming the HfO@sub 2@ layer on HfSi@sub x@O@sub y@. In this work, we investigated the physical and electrical properties of the HfO@sub 2@/HfSi@sub x@O@sub y@ prepared by a simple method; that is, the oxidation of sputtered Hf metal films on Si followed by N@sub 2@ annealing. Thin Hf layers were directly deposited on Si substrate by sputtering. The oxidation and annealing were performed at 500 °C for 120 min and in N@sub 2@ ambient at 500 °C for 60 min in furnace, respectively. Al gate was thermally evaporated on the HfO@sub 2@ film using a shadow mask. Using the TEM, AES, and XPS techniques, we confirmed that the oxidation of the thin Hf films on Si results in a HfO@sub 2@/HfSi@sub x@O@sub y@ stack layer. In addition, the thickness of an amorphous HfSi@sub x@O@sub y@ layer (HfO@sub 2@ layer) reduces (increases) after the post-oxidation annealing in N@sub 2@ ambient, which causes the increase of the effective dielectric constant. The hysteresis window and the interface state density of HfO@sub 2@/HfSi@sub x@O@sub y@ were less than 10 mV and ~3x10@super 11@ /cm@super 2@ eV without PMA, respectively. The leakage current was also low (1x10@super â€“5@ A/cm@super 2@ at 2 V). It is believed that these excellent results were obtained due to existence of the amorphous HfSi@sub x@O@sub y@ buffer layer. We also found that the degradation of HfO@sub 2@/HfSi@sub x@O@sub y@ gate oxides is more severe when electrons were injected from the gate electrode.

DI1-MoP8 Interface Formation and Electrical Properties of TiN@sub x@ (Titanium Nitride)/HfO@sub 2@/Si Structure for Application in Gate Electrode*, **Y.S. Ahn**, K.J. Kim, S.H. Ban, N.-E. Lee, S. Yang, K. Roh, Y.H. Roh,* Sungkyunkwan University, Korea

Recent extensive research activities on HfO@sub2@ as a high-k gate dielectric material are focused on the layer formation and interfacial properties between HfO@sub2@ and Si substrate. For the integration of HfO@sub2@ in MOS structures, metals as gate electrode materials are expected to be required. One of candidates for metal gate electrode is CVD tungsten. For application of CVD-W as a gate electrode, a diffusion barrier such as TiN@subx@ are often necessary to avoid the chemical etching of gate dielectrics by F atoms in the CVD precursor gas, WF@sub6@, resulting in increased leakage current. In this work, interface formation and electrical properties between TiN@subx@ and HfO@sub2@ for application of gate electrode were investigated as a function of annealing temperature. Hf layers were deposited on n-type Si(001) using rf magnetron sputter deposition. HfO@sub2@ layers of 6-7 nm thickness were formed at 500 °C by a thermal oxidation of the Hf layers for 120 min in furnace with O@sub2@ ambient. Further thermal annealing at 500 °C in N@sub2@ ambient for 60 min was carried out in order to reduce the fraction of silicate glasses formed. Then, TiN@subx@ layers of 100 nm were deposited at room-temperature by reactive d.c magnetron sputtering using Ar and N@sub2@ mixed in flow ratios of 6:1 and 6:3 at the working pressure of 4x10@super-3@ Torr and at the source power of 100 W. Phase identification of TiN@subx@ layers before and after thermal annealing of TiN@subx@/HfO@sub2@/Si at 650, 750, and 850°C in furnace, respectively, was carried out by XRD. Depth profiling analysis of Ti, Si, Hf, N, and O element for TiN@subx@/HfO@sub2@/Si structure was performed by Auger electron spectroscopy (AES). Sheet resistances of TiN@subx@/HfO@sub2@/Si systems were measured by a four-point probe. The interfacial reaction of TiN@subx@/HfO@sub2@ will be discussed by measuring the chemical binding states at the interface using XPS.

DI1-MoP9 Deposition and Characterization of Thin ZrO@sub2@ Films*, **L. Koltunski**, R.A.B. Devine, R. Marquardt,* University of New Mexico

Amorphous films of ZrO@sub2@ up to ~ 100 nm thick have been deposited on Si substrates at room temperature using O@sub2@ and Zr(C@sub4@H@sub9@O)@sub4@ source gases in an electron cyclotron resonance excited plasma enhanced chemical vapor deposition reactor working in the pressure range ~ 2 millitorr. The film composition was measured by X-ray emission and found to be stoichiometric (ZrO@sub2@) within experimental error. The refractive index at 632.8 nm was ~ 1.74 - 1.84 whilst the dielectric constant, measured on metal-oxide-semiconductor capacitor structures, was ~ 20. Glancing incidence X-ray scattering was used to ascertain the film density which was ~ 5 g cm@super-3@ as compared to a monoclinic, crystalline value ~ 5.83 g cm@super-3@. Infrared absorption spectroscopy of the amorphous films evidenced a strong transverse optic mode at 410 cm@super-1@ and an associated longitudinal optic mode at 693 cm@super-1@. From the transverse/longitudinal optic mode splitting we determine that the dielectric constant is > 11. Since the experimental value is ~ 20 other transverse/longitudinal modes must be present but not observed in the spectral range we have examined (350 - 1600 cm@super-1@). Evidence for crystalline phases (monoclinic and tetragonal) was found in the infrared spectra of samples deposited using radio frequency substrate bias. The presence of crystalline inclusions was confirmed by X-ray scattering analysis. The amorphous film dielectric constant is only ~ 9% smaller than the crystalline value (~22) whereas the refractive index is smaller by 16-21 %. The origin of these differences will be discussed.

DI1-MoP10 Material and Electrical Characteristics of ZrO@sub 2@ Film Obtained by Electron Cyclotron Resonance Plasma Enhanced Chemical Vapor Deposition (ECR-PECVD)*, B.O. Cho, **J. Wang**, S.X. Lao, J.P. Chang,* University of California, Los Angeles

ZrO@sub 2@ is investigated in this work to replace SiO@sub 2@ as the dielectric material in metal-oxide-metal (MOM) capacitors in dynamic random memory (DRAM) devices for its high dielectric constant, good thermal stability, excellent conformality, and large bandgap. ZrO@sub 2@ films were deposited on p-Si (100) wafers by ECR-PECVD method using zirconium tetra-tert-butoxide (Zr(OC@sub 4@H@sub 9@)@sub 4@) as an organometallic precursor, Ar as a carrier of the precursor vapor, and O@sub 2@ as an oxidant. X-ray photoelectron spectroscopy and secondary ion mass spectrometry indicated that stoichiometric ZrO@sub 2@ film was obtained with various amount of carbon incorporation depending upon the electron temperature and the O@sub 2@/Ar flow rate ratio. X-ray diffraction showed that the films deposited without substrate heating were amorphous. By manipulating the negative substrate bias and raised the deposition temperature to around 400 °C, carbon-free amorphous ZrO@sub 2@ was obtained. High resolution transmission electron microscopy was used to observe the interfacial thin film formation between the deposited ZrO@sub 2@ and the substrate Si. The electrical property of the as deposited ZrO@sub 2@ was assessed by forming Al/ZrO@sub 2@/Si capacitor structures. Good capacitance-voltage and current-voltage characteristics were obtained with k=22 at 1 MHz and J=4x10@super -5@ A/cm@super 2@ at -1.5 V, respectively. The C-V response showed a small hysteresis of <60 mV and an interfacial state density of 2x10@super 11@ cm@super -2@ eV@super -1@ based on capacitance measurement at various frequencies. The influences of carbon incorporation, substrate heating and biasing, and post-annealing on the bulk and the interfacial trap formation were investigated by photoconductivity measurement, which enables the determination of leakage conduction mechanism.

DI1-MoP11 Characteristics of Zirconium Oxide with Different Gate Electrodes*, **S.-W. Nam**, J.-H. Yoo, D.W. Lee, D.-H. Ko,* Yonsei University, Korea*; J.-H. Ku,* Samsung Electronics Co., Korea*; M.-H. Cho,* Yonsei University, Korea*; S. Choi,* Samsung Electronics Co., Korea*; C.-W. Yang,* Sungkyunkwan University, Korea

MOS devices are being continuously scaled, especially the gate oxide thickness and the source/drain junction depth. Key process issues in conventional SiO@sub 2@ scaling are with the gate stack, including boron penetration and gate leakage for very thin gate oxides and depletion effects in the polysilicon electrodes. The solution is to use a gate dielectric with a higher dielectric constant than that of SiO@sub 2@. Together with a high-K dielectric, dual metal gate may be implemented to enable the scaling of MOS devices. We investigated the electrical properties and thermal stability on sputtered ZrO@sub 2@ films with various electrodes for p-type silicon substrate. ZrO@sub 2@ thin films as a gate dielectric were deposited by reactive dc magnetron sputtering, followed by thermal annealing in either O@sub 2@ or N@sub 2@ using furnace. And then various metals such as Al, Pt, TiN, TiN/Al, and TiN/Pt were deposited by sputtering as a gate electrode. Also, conventional poly-Si and poly-SiGe as a gate electrode were deposited by chemical vapor deposition. By HRTEM and XPS analyses, we evaluated compatibility and thermal stability between the ZrO@sub 2@ films and electrodes. We focused on the interfacial layer between high-k dielectric and electrodes. In comparison with Pt electrode, the accumulation capacitance of the MOS with Al electrode demonstrated about 8% degradation. And we compared electrical characteristics of Al (or TiN/Al) and Pt (or TiN/Pt) with other well-known gate electrodes such as poly-Si and poly-SiGe.

DI1-MoP12 Diffusion Studies of High k Gate Dielectric Candidates Hafnium and Zirconium Silicates into Si*, **M.A. Quevedo-Lopez**, M. El-Bouanani, S. Addepalli, C. Huang, J.L. Duggan, B.E. Gnade, R.M. Wallace,* University of North Texas*; L Colombo, M. Bevan, M. Douglas, M. Visokay,* Texas Instruments Inc.

The area of advanced gate dielectrics has gained considerable attention recently because the SIA technology roadmap predicts the need for a <2.0 nm SiO@sub 2@ gate dielectric for sub-0.13 mm scaled silicon CMOS.@footnote 1@ Desirable properties for new gate dielectrics include; higher permittivity (@kappa@) than SiO@sub 2@ (@kappa@ = 3.9), minimal reaction barrier, thermodynamic stability in direct contact with silicon, low leakage current (<1 A/cm@super 2@ at 1V), and very low diffusion into silicon. Considering these requirements, Hf silicate and Zr silicate have been proposed as suitable candidates for advanced gate dielectric applications.@footnote 2,3@ However, more issues have to be resolved. Among those issues metal diffusion (Zr, Hf) into the channel is critical because impurity diffusion from the gate dielectric into the channel region would likely result in deleterious effects on carrier mobility. We have studied the diffusion of Hf and Zr from high-@kappa@ gate dielectric candidates HfSixOy and ZrSixOy. The studies were carried out after aggressive thermal annealing followed by chemical etching. The annealed/etched films were studied using monochromatic X-ray Photoelectron Spectroscopy (XPS), Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), High resolution TEM, and Rutherford Backscattering Spectrometry (RBS). Film deposition, chemical etching and characterization issues are discussed. No detectible Hf diffusion into Si from RTP and furnace-annealed films is observed. In contrast Zr diffusion is observed upon RTP and furnace anneals. Implications for high-k gate dielectric applications are also discussed. This work was supported by the Texas Advanced Technology Program, the Semiconductor Research

Corporation, and DARPA. @FootnoteText@@footnote 1@Semiconductor Industry Association roadmap 1999 @footnote 2@G.D. Wilk and R.M. Wallace, Appl. Phys. Lett. 74, 2854 (1999). @footnote 3@G.D. Wilk and R.M. Wallace, Appl. Phys. Lett. 76, 112 2000). @footnote 4@W.-J. Qi, et al., Appl. Phys. Lett. 77, 1704 (2000).

DI1-MoP13 High-dielectric Constant Aluminum Oxide Films*, **C. Falcony,*** CINVESTAV and ESFM-IPN, Mexico*; M. Aguilar-Frutis,* CICATA-IPN, Mexico*; J. Guzman,* CICATA-IPN, IIM-UNAM, Mexico*; M. Garcia,* IIM-UNAM, Mexico

Aluminum oxide films deposited by Spray Pyrolysis at low temperatures (450 to 650°C) have been studied as high-K dielectric layers on silicon. Dielectric constants in the range of 6.7 to 8.5 and interface states in the order of 10@super 11@ at midgap have been obtained. Overall optical, electrical, and structural characteristics are strongly dependent on the deposition parameters, as well as the presence of carbon as impurity. Dielectric breakdown for these films is larger than 5 MV/cm.The electrical conduction mechanisms are discussed.

DI1-MoP14 UHV-CVD of Al@sub 2@O@sub 3@ for Gate Dielectric Applications*, B.R. Rogers, **Z. Song**, R.D. Geil, T.P. Hanusa, R.A. Weller,* Vanderbilt University

Successful replacement of silicon dioxide-based MOSFET gate dielectrics by a high-permittivity (high-k) dielectric is a critical step in the continued drive to build the smaller, faster, lower-power, more-integrated circuits that society is demanding. Our goal toward this effort is to develop a thermodynamically and microstructurally stable, amorphous material system, having no interfacial silicon dioxide formation. In this presentation we will discuss our work on developing alumina/zirconia alloys for use as gate dielectrics. We have begun this effort by studying the deposition of alumina films in an ultra-high-vacuum chemical vapor deposition (UHV-CVD) system. We use a precursor of a mixed alkyl alkoxide aluminum dimer. This compound contains triethyl (tri-sec-butoxy) dialuminum, tetraethyl (di-sec-butoxy) dialuminum, and diethyl (tetra-sec-butoxy) dialuminum. This mixture is non-pyrophoric and is less susceptible to hydrolysis than other tialkoxide aluminums. Our studies have included total deposition pressures between 10@sup -5@ and 10@sup -3@ torr, and substrate temperatures between 350 and 500 °C. In addition we will discuss the characterization of these films using time-of-flight medium energy ion scattering (ToF-MEIS), a characterization capability unique to Vanderbilt University. . @FootnoteText@ This work is supported by the National Science Foundation grant # CTS-0092792.

DI1-MoP15 Annealing Effects of Al@sub 2@O@sub 3@ Films Grown on Si(100)*, **Y.S. Roh**, M.-H. Cho, Y.K. Kim, S.A. Park, D.-H. Ko, C.N. Whang, K.H. Jeoung,* Yonsei University, Korea

The annealing effects of the thin Al@sub 2@O@sub 3@ films grown on Si(100) by sputtering method was deeply investigated using various physical and electrical measurement methods. All the films grown in the temperature below 300@super o@C using sputtering Al@sub 2@O@sub 3@ target showed amorphous structure as examined by x-ray diffraction and transmission electron microscopy. The amorphous structure was maintained up to 600@super o@C and then transformed to @gamma@-Al@sub 2@O@sub 3@ phase above the annealing temperature of 600@super o@C . In particular, the characteristics of the leakage current density in MOS structure depended on the annealing temperature. The densification of the film due to the crystallization resulted in improved electrical characteristics; the crystallization enhanced the improvement of the dielectricity and breakdown field strength. Moreover, the depth profiling data using XPS showed that the improvement of the leakage properties in Al@sub 2@O@sub 3@ film closely related with the change of interfacial layer under the high temperature annealing. In particular, the fixed trap density was increased even after the annealing process, which resulted from the difference of the chemical state of the Al@sub 2@O@sub 3@ film along with the structural change.

DI1-MoP16 Studies on Ta@sub 2@O@sub 5@ Thin Films Deposited on Si(100) by MOCVD and Sputtering Techniques*, P. Passacantando, L. Lozzi, V. Salerni, P. Picozzi, **S. Santucci,*** University of L'Aquila, Italy

Tantalum oxide is one of the most promising dielectric materials to be used for high performance in integrated circuits and electronic packaging applications. In this work stoichiometric Ta2O5 thin films have been successfully grown on Si(100) substrate by metal-organic chemical vapor deposition (CVD) technique using tantalum ethoxide (Ta(OC2H5)5) as precursor and by DC sputtering in reactive Ar/O2 atmosphere. The growth rate, the stoichiometry, the surface morphology and the structural properties of the films growth with and without nitrogen passivation of the silicon substrate, have been studied by X-Ray Reflectivity (XRR), X-ray Photoelectron spectroscopy (XPS), Atomic Force Microscopy (AFM) and X-ray Diffraction (XRD). We observed how the formation of a SiO2 layer between the silicon substrate and the Ta2O5 deposited film is nearly totally inhibited by a pre-treatment at 750Â°C in NH3 flux of the H-terminated silicon surface before the Ta2O5 deposition. Furthermore, we observed that a post growth annealing in a O2/N2 mixture up to 850Â°C determines a lowering of the leakage current whose dominating mechanism has been attributed to trap assisted Frenkel-Poole emission.

DI1-MoP17 Microstructure of BaTiO@sub3@ Films Prepared by Electrochemical Depostion on Ti-Coated Silicon Substrates*, **C.-T. Wu,*** National Chung Hsing University, Taiwan*; F.-H. Lu,* National Chung Hsing University, Taiwan, Taiwan, R.O.C.

Crystalline BaTiO@sub3@ films were directly synthesized onto Ti-coated silicon substrates in highly alkaline condition at 55°C using Ba(OH)@sub2@ or Ba(CH@sub3@COO)@sub2@ as electrolyte. Titanium films were first deposited by Filtered Cathodic Arc Deposition (FCAD) of varying thickness about 0.2 µm, 2µm and 5µm onto silicon wafer. The electric charge of electrolysis was carefully controlled to grow appropriate thickness of BaTiO@sub3@ films by applying a anodic oxidation method. From previous studies using pure Ti plates as substrates, we prepared the films by the potentiodynamic method to the preset voltages. X-ray diffraction results showed cubic BaTiO@sub3@ phase could be present at low electrolytic voltage of 3 V and higher voltage of 75 V. The BaTiO@sub3@ films synthesized at 3 V develops uniformly distributed spherical like small particles, and crater-shaped and large-grained BaTiO@sub 3@ films were observed at 75 V. The great differences of morphology between these two electrolytic conditions were also verified by surface roughness measurements. SEM/EDS, AES and XPS were used to analyze the composition of BaTiO@sub3@ films. The growth mechanisms of BaTiO@sub3@ films were also discussed.

DI1-MoP18 Electrical Properties of BST Thin Films on Si Substrates*, **N.A. Suvorova**, A.H. Mueller, E.A. Irene,* University of North Carolina, Chapel Hill*; O. Auciello,* Argonne National Laboratory*; J.A. Schultz,* Ionwerks, Inc.

Among many materials with high dielectric constant for use in advanced MOSFET's, Ba@sub 0.5@Sr@sub 0.5@TiO@sub 3@ (BST) is one of the most promising candidates, since it has a static dielectric constant over 300 for bulk material. However, BST thin films always exhibit much lower dielectric constant. The formation of interfacial layers between BST and Si substrate results in reduction of the overall dielectric constant that dramatically decreases the capacitance of the stack. Our BST thin films studies@footnote 1@ have included in-situ real time material characterisation as well as ex-situ material and electronic characterizations. The present study focuses on electronic characterization of Al/BST/p-Si and Ir/BST/p-Si structures with and without intervening SiO@sub 2@ layers between BST and Si substrate. Among the electronic measurements included are the dielectric constant and leakage current of the BST thin films as well as interface charges. Attepmts will be made to correlate the electronic properties with the material characteristics that will be presented separately.@footnote 1@ @FootnoteText@ @footnote 1@ A.H. Mueller, N.A. Suvorova, E.A. Irene, O. Auciello, and J.A. Schultz. In-situ, real time studies of interface formation of BST thin films on Si substrates. Present Conference Proceedings.

DI1-MoP19 Thermal Decompostion Mechanisms of (Ba,Sr)TiO@sub 3@ Film Precursors*, **J.P. Senosiain**, C.B. Musgrave,* Stanford University

Next-generation memory devices will require high-permittivity dielectric materials able to handle sufficient charge as the dimensions of memory cells continue to scale down. Barium strontium titanate (BSTO) is a strong candidate for such applications, with a dielectric constant many times higher than that of the presently used silicon oxy-nitrides. To grow BSTO thin films effectively, a basic understanding of the precursor chemistry and deposition mechanism is needed, yet the literature in this areas is quite scarce. We have employed Density Functional Theory (DFT) and pseudopotential basis sets to study the thermal decomposition mechanisms of the @beta@-diketonate precursors: Ba(thd)@sub 2@, Sr(thd)@sub 2@ and Ti(OH)@sub 2@(thd)@sub 2@. In all these species, we find the metal-oxygen bond to be the weakest and thus the first to be broken. The cleavage of a second metal-oxygen bond leads to considerable geometric rearrangement and is energetically favourable. This is followed by the detachment of tert-butyl radicals and possible ring-closing reactions. Other decomposition channels, as well as their implications to the deposition process, are discussed in terms of their thermochemistry.

DI1-MoP20 Enhancement of Etching Characteristics of (Ba,Sr)TiO@sub 3@ Using Magnetically Enhanced Inductively Coupled CF@sub 4@/Ar Plasma*, D.P. Kim, C.I. Kim,* Chung-Ang University, Korea*; **T.H. Kim,*** Yeojoo Institute of Technology, Korea*; Y.J. Seo,* Daebul University, Korea*; E.H. Kim,* Cheju National University, Korea*; E.G. Chang,* Chung-Ang University, Korea

Now, three major trends in IC device fabrication are putting more functions on individual chips, fabricating faster chips, and lowering IC fabrication costs. Smaller memory cell increases its speed with using other materials sets like metal gates and electrodes, and high-k dielectrics. Ferroelectric (Ba,Sr)TiO@sub 3@ (BST) thin film have been attractive for advanced dynamic random access memories (DRAMs) applications due to its high dielectric constant. The smaller features need better plasma-etching processes to ensure etch fidelity and new features. Because the etch rate of BST thin film is low in a reactive ion etcher and an inductively coupled plasma etcher, magnetically enhanced inductively coupled plasma (MEICP) was used. Plasma density of MEICP is higher than that of RIE and ICP. In this study, BST thin films were etched in CF@sub 4@/Ar. The experiments were carried out with measuring etch rates and selectivity as a function of gas mixing ratio, rf power, dc bias voltage and chamber pressure. The maximum etch rate of BST thin film was 1800 Å/min at CF@sub 4@(10)/Ar(90), rf power of 600W, dc voltage of -300V, and chamber pressure of 5 mTorr. The selectivities of BST to Pt and photoresist were 0.6 and 0.7, respectively. The chemical states on the etched surface were investigated with x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used to investigate the surface morphology of BST thin films exposed in plasma. X-ray diffraction (XRD) was evaluated to investigate physical properties of BST before and after etching process. Electrical property was characterized by measuring leakage current.

DI1-MoP21 Structural and Microwave Properties of Artificial BaTiO@sub 3@/SrTiO@sub 3@ Superlattice on MgO and SrTiO@sub 3@ Substrate by Pulsed Laser Deposition*, **J.H. Kim**, L. Kim, Y.N. Kim, D. Jung, Y.S. Kim, J. Lee,* Sungkyunkwan University, Korea

BaTiO@sub 3@ (BTO)/SrTiO@sub 3@ (STO) superlattice has been deposited on MgO and STO substrates by pulsed laser deposition (PLD). BTO/STO superlattice has an epitaxial layer of BTO and STO with the parallel crystallographic orientation to MgO or STO substrates. The periodicity of the BTO/STO superlattice was varied from 0.8 nm thickness to 50 nm and the total thickness of the superlattice was fixed at 100 nm. Structural properties of the superlattice with various periods were examined by X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM). This superlattice exhibited ferroelectricity in capacitance-voltage (C-V) characteristics, i.e., inverted butterfly hysteresis loop. Asymmetric behavior in C-V characteristics were also observed in the superlattice, which had different bottom and top electrodes each other. For microwave applications, the voltage tunability in the C-V characteristics was measured. The voltage tunability increased with decreasing the period of the superlattice. The tunability reached 90 % at the period of 2 nm. The tunability of BTO/STO superlattice was discussed in terms of periodicity and strain relaxation.

DI1-MoP22 Ferroelectric PMNT Thin Films Deposited on TiN:O@sub 2@ by Laser Ablation*, **J.M. Siqueiros,*** UNAM, Mexico*; A. Fundora, J. Portelles,* Universidad de La Habana, Cuba

Pb(Mg@sub 1/3@Nb@sub 2/3@)@sub0.9@Ti@sub 0.1@O@sub 3@ (PMNT) polycrystalline thin films were deposited on TiN/Si substrates at different temperatures by laser ablation, using a wavelength of 248 nm, 30 ns pulse duration, 10 Hz repetition rate and a fluence of 2 J/cm@super 2@. As a result of this previous study, it was determined that deposits at 250 @super 0@C in a 200 mTorr oxygen atmosphere gave the best results with a post annealing treatment at 500 @super 0@C where a PMNT perovskite single phase formation was confirmed by x-ray diffraction (XRD) analysis. Higher and lower annealing temperatures presented a secondary pyrochlore phase. The electrical properties and the influence of the annealing temperature on the dielectric properties of the PMNT thin films were characterized through P-E hysteresis. Fatigue measurements were used to evaluate the long-term performance of the PMNT/TiN/Si system. The characteristics of the TiN films used as bottom electrodes were evaluated using Auger Electron Spectroscopy (AES) and Transmission Electron Microscopy (TEM) with particular emphasis in the interfaces. @footnote 1@ This work has been partially supported by CoNaCyT-Mexico, through grant No. 33586E and by DGAPA-UNAM grant No. IN104000. The technical support by I. Gradilla, E. Aparicio, V. Garcia and F. Ruiz is acknowledged.

Dielectrics
Room 134/135 - Session DI2-MoP
Low K Dielectrics Poster Session

DI2-MoP1 Deposition of Si-C-O-H Alloy Dielectric Films as a Low Dielectric Permittivity Insulators*, **B.K. Hwang**,* Dow Corning Corporation*; M.J. Loboda,* Wacker Siltronic Corporation*; W.D. Gray, G.A. Cerny, R.F. Schneider, J.A. Seifferly, D.W. Roehl,* Dow Corning Corporation

As the feature size in ultra large scale integrated circuit (ULSI) decreases, the minimization of interconnect resistance - capacitance (RC) coupling through the use of copper interconnect metalization and low dielectric permittivity (low-k) has become an intensive interest to the semiconductor industry. Among many low-k candidate materials, carbon-doped silicon oxides, i.e., Si-C-O-H alloy dielectric films have been investigated. These films can be deposited by plasma enhanced chemical vapor deposition (PECVD) of organosilicon gas, (CH3)xSiH4-x, and oxidant mixtures. In this study, we will present the structure, composition, and electrical characteristics of PECVD Si-C-O-H films with different process parameters. The precursor gas mixture used in this study is the trimethylsilane (Dow Corning Z3MS(TM), Semiconductor Grade), oxygen (O2), and helium (He). Samples of Si-C-O-H films were deposited on silicon wafers using a 200mm PECVD reactor. Rutherford backscattering spectrometry and hydrogen forward scattering spectrometry (RBS/HFS), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) were evaluated to understand the composition and structure of films. The electrical properties such as a dielectric constant, leakage current density, and dielectric breakdown voltage were tested with a metal-insulator-silicon (MIS) structure. The typical film properties of this study are as follows: (1) FTIR spectra indicate that the hydrogen and carbon are incorporated in the form of Si-(CH2)n-Si, Si-H, Si-CH3, and Si-C into a SiO2 backbone. (2) Composition of Si-C-O-H film : Si / O / C / H = 0.2 / 0.36 / 0.12 / 0.32 (based on RBS/HFS). (3) Bulk film density : 0.97 (g/cm3). (3) Dielectric constant (k) at 1MHz : 2.7 ~ 3.2 and k value has a strong relationship with Si-OH content. (5) Leakage current density : 3x10-10 (A/ cm2) at 0.5 (MV/cm) (6) Dielectric breakdown field : > 4 (MV/cm).

DI2-MoP2 Characterization of Plasma-CVD Grown Low-k Porous Silica Films using Positron-annihilation Lifetime Spectroscopy*, **T. Ohdaira**, R. Suzuki,* National Institute of Advanced Industrial Technology (AIST), Japan*; Y. Shioya,* Semiconductor Process Laboratory Co., Ltd., Japan*; T. Ishimaru,* Canon Sales Co. Inc., Japan

Positron-annihilation lifetime spectroscopy was used to determine the pore size distributions in low-k porous silica films deposited by plasma-enhanced chemical vapor deposition (PE-CVD) with source gases of hexamethyldisiloxane (HMDSO) and nitrous oxide (N@sub 2@O). In PE-CVD, the porosity of the film can be controlled by the deposition conditions, e.g. the pressures and flow rates of the source gases. In the present study, several kinds of porous films with k values ranging from 2.6 to 3.2 were prepared. The positron-annihilation lifetimes at selected depths in the porous films (500 nm thick) were measured by using a mono-energetic pulsed positron beam (0.5 keV - 20 keV). The obtained results show that the pores with average volumes of 0.3 - 1.1 nm@super 3@ are introduced in the films, and that the pore size strongly depends on the deposition conditions. The correlation between the pore size and the dielectric constant will be discussed.

DI2-MoP3 Plasma-Reacting Behaviour of Spin-on Hybrid Organic Siloxane Polymer (HOSP) Low-Dielectric-Constant Thin Films*, **S.-T. Chen**, G.-S. Chen,* Feng Chia University, Taiwan*; T.-C. Chang,* National Sun Yat-Sen University, Taiwan*; C.-P. Liu,* National Cheng Kung University, Taiwan

This work employs Fourier transform infrared spectroscopy and Raman spectroscopy, along with atomic force and transmission electron microscopies to examine microstructure and bonding stabilities of spin-on hybrid organic siloxane polymer (HOSP) low-dielectric-constant (k) thin films after they are exposed to oxygen ashing and (or) various passivating plasma treatments. The spectroscopic and microscopic analyses reveal that, upon exposure to the oxygen plasma, the Si-CH@sub 3@ and Si-C bonds inherent in the thin HOSP (k = 2.5) film are disrupted substantially and, subsequently replaced by highly polarized Si-O, Si-H and (or) Si-OH bonds. These replacements thus degrade the HOSP dielectric film by increasing the magnitude of k significantly. Preliminary results indicate that the HOSP film can be strengthened by passivating it in an adequate plasma. Doing so allows the HOSP to be treated by oxygen-plasma ashing while still maintaining a fairly stable bonding and dielectric properties. Finally, the capability of several ultra-thin (<= 5 nm) capping layers in retarding copper diffusion into the HOSP dielectric layer will be evaluated by measuring C-V and I-V curves of Si/HOSP/capping layers/Cu capacitor samples under conditions of biased thermal stress of 2-4 MV/cm and 150-250 °C.

DI2-MoP4 Process Characterization of Low Dielectric Constant Silicon Containing Fluorocarbon Films by Plasma Enhanced Chemical Vapor Deposition*, **Y.Y. Jin,*** Louisiana State University*; H. Kim,* Kyungpook National University, S. Korea*; G.S. Lee,* Louisiana State University

The development of low dielectric constant (low-k) materials has become one of the most important key challenges for interlayer dielectrics (ILD) of the high performance ultra-large-scale-integration (ULSI) devices. As the decreased design rule and increased complexity of ULSI circuits have essentially increased the crosstalk and RC time delay caused by parasitic capacitance, a great deal of effort has been spent in reducing the dielectric constant of the interlayer as well as reducing the resistance of the wiring metals. Silicon containing fluorocarbon (SiCF) thin films for use as low dielectric ILD have been investigated. The SiCF films were deposited with plasma enhanced chemical vapor deposition (PECVD) using 5% disilane in helium (5%Si2H6/He) and carbon tetrafluoride (CF4) as the precursors. The properties of SiCF films effected by the total flow, the flow rate ratio of CF4/Si2H6 and annealing were investigated to obtain optimal deposition. This work presents the results of a process characterization of PECVD which are the deposition rate, the refractive index and the roughness as functions of the total flow and the flow ratio, and the shrinkage rate and the dielectric constant before/after annealing.

DI2-MoP5 Etching Characteristics of Polyimide Film as Interlayer Dielectric Using Inductively Coupled Plasma*, **P.S. Kang,** C.I. Kim,* Chung-Ang University, Korea*; S.G. Kim,* ETRI, Korea*; H.S. Choi,* Juseong College, Korea*; C.I. Lee,* Ansan College of Technology, Korea*; E.G. Chang,* Chung-Ang University, Korea

In ultra-large-scale integrated circuits, where critical dimensions continue to shrink into the deep submicrometer range, RC constant becomes an increasingly dominant factor in governing both the velocities of operation and the corresponding power consumption. One method to reduce RC constant is the reduction of the dielectric constant of the intermetal material. Therefore, many low-k materials such as amorphous carbon, Teflon, SiOF, Polyimide have been studied by the various research institutes. Among them polyimide (PI) films are widely due to low dielectric constant ,low water absorption, high gap-fill and planarization capability. In this study, etching characteristics of polyimide film with O@sub 2@/CF@sub 4@ gas mixing was studied using inductively coupled plasma (ICP). The etch rate and selectivity were evaluated to rf power, dc-bias voltage, chamber pressure, and substrate temperature. High etch rate (over 10000Å/min) and vertical profile was acquired in CF@sub 4@/(CF@sub 4@+O@sub 2@) of 0.2. The selectivities of polyimide to PR and SiO@sub 2@ was 1.1, 34, respectively. The profiles of polyimide film etched in CF@sub 4@/O@sub 2@ were measured by a scanning electron microscope (SEM) with using an aluminum hard mask pattern. The chemical states on the PI film surface were measured by x-ray photoelectron spectroscopy (XPS). Ion current density and plasma density of O radical and fluorine in O@sub 2@/CF@sub 4@ were investigated by Langmuir probe and optical emission spectrometer (OES). After the etching process, leakage current and dielectric constant were characterized by semiconductor parameter analyzer (HP4145B) and impedance analyzer (HP 4192 at 1MHz) using Al/PI/Al capacitor.

DI2-MoP6 An Opportunity to Study the Outgassing Behavior of a Novel Organic Low K Material*, **J.F. Bernard,** S. Pangrle, C. Gabriel,* Advanced Micro Devices

Lowering interlayer dielectric(ILD) capacitance is key to enjoying the benefits of further advances in IC design and Cu interconnect technology. Conventional SiO2 is now being replaced as an ILD by an array of new materials. In some cases porosity is used to lower k, in others the films are actually novel organic materials. These new low k dielectrics can behave very differently from the SiO2 used in conventional IC fabrication to date. Outgassing is one metric that is a direct measure of film stability, curing, and contamination. Organic films especially can exhibit significant changes in outgassing vs. etch, cleaning and thermal budget. This complex outgassing of organics due to or during processing is a definite departure from SiO2, even for organo-precursor based glasses such as TEOS. We at AMD have had the opportunity to extensively study the outgassing behavior of DOW Chemical's organic low k, SiLK, with both Dynamic and Isothermal Evolved Gas Analyses(EGA). Two distinct regimes of outgassing were observed. At lower temperature atmospheric contaminants are dominant. Benzene related film outgassing was observed above 450°C. XPS analyses confirmed the presence of aromatic binding. The stability of SiLK with respect to various processing steps was investigated with interesting results. These investigations led us to also take a look at our wafer storage materials. The affinity for the absorption of organics was demonstrated and minimized. The effects of processing on a porous derivative were examoned with an etch and clean matrix. Overall evolved gas analyses are proving to be a key data point in understanding and, ultimately, utilizing low k films in advanced IC fabrication.

DI2-MoP8 The Effect of Hydrogen Plasma Treatment on Low-k Hybird-Organic-Siloxane-Polymer (HOSP) Against Damage During Photoresist Removal*, T.C. Chang,* National Sun Yat-Sen University, Taiwan, R.O.C.*; Y.S. Mor,* National Chiao Tung University,Taiwan, R.O.C., Taiwan, R.O.C.*; **P.T. Liu,*** National Nano Device Laboratory, Taiwan, R.O.C*; T.M. Tsai, C.W. Chen,* National Chiao Tung University, Taiwan, R.O.C.*; W.C. Gau,* National Tsing Hua University, Taiwan, R.O.C.*; S.M. Sze,* National Chiao Tung University, Taiwan, R.O.C.

While critical dimensions continue to shrink into the deep submicron range for the need of ULSI circuit, the RC constant that governs both the parasitic delay time (i.e. the speed of operation) and corresponding power dissipation, becomes a dominant factor in improving the chip performance. An organic SOG, the Hybird-Organic-Siloxane-Polymer (HOSP) has high evaluation in ULSI applications because of the low dielectric constant about 2.5. It is also one suitable material of Methyl-Hybrido-Silsesquioxane (MHSQ) films, and simultaneously has good gap filling, low stress and comparable enough strength etc. Face with the same issues of organic low k materials, however, the quality of HOSP film is degraded after photoresist removing. This instability is one of the major problems in using HOSP as a low-k material. In this study, the HOSP film has been investigated for the intermetal dielectric application. In addition, H@sub 2@ plasma pre-treatment was applied to HOSP films. This treatment prevents HOSP films from O@sub 2@ plasma and chemical wet stripper damage during photoresist stripping processes. In the H@sub 2@ plasma treatment, hydrogen radicals can passivate the HOSP surface, preventing the formation of Si-OH bonds so that moisture uptake can be avoided. In addition, dielectric degradation due to photoresist stripping process can thereby solve by H@sub 2@ plasma treatment. These experimental results indicate that H@sub 2@ plasma treatment is a promising technique for integrating the HOSP as intermetal dielectric application.

Electrochemistry and Fluid-Solid Interfaces
Room 134/135 - Session EC-MoP
Poster Session

EC-MoP1 Ex situ and In situ Investigations of Dilute Perchloric Acid on Cu(111)*, **M. Duisberg,** P. Wahl, B. Obliers, J. Hommrich, P. Broekmann, K. Wandelt,* University of Bonn, Germany

In electrochemistry perchloric acid is assumed to be a prototype for an inert electrolyte. This statement, however, turns out to be not correct for copper electrode surfaces. In this study we present combined in-situ and ex-situ mesurements illustrating the surface electrochemistry of a Cu(111) electrode exposed to a dilute perchloric acid electrolyte. The initial cyclic voltammogram (CV) of an UHV prepared Cu(111) single crystal in 10 mM HClO@sub 4@ shows a reversible pair of peaks at 180 mV vs RHE. After a few cycles this CV changes into a CV identical to that directly obtained after an electropolishing preparation procedure which does not show this reversible pair of peaks. Additional to this fast change there is a long time instability of the CV. A prolonged cycling of the potential leads to the formation of a cathodic peak at -220 mV and a smaller anodic peak at 190 mV. Additionally the onset of hydrogen evolution is shifted towards cathodic potentials by 60 mV in comparison to the initial CV. In-situ STM measurements of Cu(111) in perchloric acid reveal a completely disordered adlayer which is present at anodic electrode potentials. The bare copper surface is not seen under these conditions as one would expect for an inert electrolyte. Ex-situ XPS and LEIS measurements indicate the presence of copper oxide species and chloride as well. The origin of this species at the surface will be discussed. At cathodic potentials near the onset of hydrogen evolution a highly ordered superstructure is observed by STM. This adlayer remains stable also under massive hydrogen evolution. Under similar conditions identical adlayers were also found in other acidic elctrolytes like sulfuric acid or hydrobromic acid, and are attributed to ordered hydronium/water layers.

EC-MoP2 Cadmium Underpotential Deposition on Cu(111): A Combined In Situ and Ex Situ Study*, **J. Hommrich**, Z. Park, C. Stuhlmann, K. Wandelt,* University of Bonn, Germany

The underpotential deposition (UPD) of Cd on the Cu(111) surface was studied through ex situ (XPS, LEIS, LEED)@footnote 1@ and in situ (CV, EC-STM) methods. Cd was deposited from an aqueous solution containing 10@super-4@M CdCl@sub 2@/10@super -2@M HCl. After deposition of a complete UPD-layer a hexagonal adlayer with a 3.8 Å lattice spacing was observed by EC-STM. This superstructure shows an additional long-range periodicity (Moiré-pattern). Two rotational domains of this Moiré-pattern can be distinguished which is in agreement with ex situ LEED measurements. XPS and LEIS measurements led to the conclusion that this rather open structure (the Cd-Cd distance in bulk Cadmium is 2.98 Å) is stabilised by an adsorbed Cl overlayer. Furthermore the initial growth of the UPD-film seen by STM is discussed: In the beginning of the UPD the growth of 2D Cd islands can be monitored by STM. The observed height of these islands and the change of the contour of the substrate steps suggest that embedding of Cd into the upper substrate terraces takes place. Polarisation experiments revealed that the current-potential desorption spectra of UPD-films depend on the polarisation time. The potential of the sample was held in the UPD regime at -370 mV vs. RHE between 1 to 90 minutes. Subsequent anodic stripping of these UPD films led to the observation of an increasing charge transfer as a function of polarisation time accompanied by a change in the form of the desorption peak. In addition a roughening of the surface was observed by STM during the anodic stripping. . @FootnoteText@ @footnote 1@ C. Stuhlmann, Z. Park, C. Bach, K. Wandelt Electrochim. Acta 44 (1998) 993.

EC-MoP3 Microscopic Structure and Reactivity of Alloyed AuPd(111) Electrode Surfaces*, F. Maroun,* Universite P & M Curie, France*; F. Ozanam,* CNRS-Ecole Polytechnique, France*; O. Magnussen, **R.J. Behm**,* University Ulm, Germany

The electrochemical and electrocatalytic properties of defined atomic Pd ensembles in a PdAu(111) surface alloy electrode, serving as model system for bimetallic electrocatalysts, were evaluated by a combination of in-situ microscopic, IR spectroscopic and electrochemical measurements, using H and CO adsorption/ oxidation as model reactions. PdAu electrodes with atomically flat surfaces and variable stoichiometry were prepared in a controlled way by electrodeposition on Au(111) under diffusion-limited conditions. The amount and distribution of Pd surface atoms was determined by atomic resolution in-situ scanning tunneling microscopy with chemical contrast. The electrochemical/catalytic properties of individual types of Pd ensembles were determined by comparison with spectroscopic and voltammetric data. This way, the critical ensembles for CO and H adsorption were identified as Pd monomers and dimers, respectively. The specific chemical properties of these ensembles as compared to bulk Pd and Pd thin-film electrodes provide a microscopic basis for understanding the distinct catalytic properties of PdAu alloys observed at the macroscopic scale.

Manufacturing Science and Technology
Room 134/135 - Session MS-MoP

Aspects of Manufacturing Science and Technology Poster Session

MS-MoP1 Investigations on Post Cu CMP Cleaning of Colloidal Silica Slurry*, T.-C. Wang, T.E. Hsieh, S.-Y. Chiu,* National Chiao Tung University, Taiwan, R.O.C.*; **Y.-L. Wang**,* Taiwan Semiconductor Manufacturing Company*; J.J. Chang,* National Chiao Tung University, Taiwan, R.O.C.*; Y.-N. Shieh,* Chang Chun Petrochemical Co., Ltd., Taiwan

Chemical mechanical polishing (CMP) is the only way to achieve the global planarization in copper damascene process. In addition to complex consumables and process controls, one of the key issues in mass manufacturing using CMP technology is post-CMP cleaning. In this study, novel clean solutions for efficient removal of colloidal silica from polished copper line were proposed. There were three kinds of formulated post Cu CMP cleaning solutions carried out including PVA, Dextrose and D-sorbitiol aqueous solution. Cleaning with these chemistries was able to change the character of the colloidal silica abrasive surface and eliminate the strong tendency of the absorption of colloidal silica on copper line. From the SEM images of polished copper surface, abrasive-free Cu surface could be obtained. Besides, the surface-scan for defect analysis performed a different level for Cu CMP post-clean efficiency. In addition, the electrical analyses for polished pattern wafers cleaning were evaluated to verify the performance of these formulated clean solutions.

MS-MoP2 In-Situ EIS Approaches to the Copper CMP Slurry Characterization*, **S.-Y. Chiu**,* National Chiao Tung University, Taiwan, R. O. C., R.O.C.*; J.-W. Hsu, Y.L. Tasi,* National Tsing Hua University, Taiwan, R. O. C.*; Y.-L. Wang,* Institute of Materials Science and Engineering, Taiwan, R. O. C.*; M.-S. Tsai,* National Nano Device Laboratories, Taiwan, R. O. C.*; H.C. Shih,* National Tsing Hua University, Taiwan, R. O. C., TAIWAN*; M.-S. Feng,* National Chiao Tung University, Taiwan, R. O. C., R.O.C.

In the chemical-mechanical polishing study, slurry chemistry in chemical-mechanical polishing of Cu thin film has been evaluated in various slurries. Various types of oxidizer and inhibitor were changed in the concentration and slurry pH were investigated. In nitric acid based slurry, with both H+ and NO3- present, it provides a corrosion environment for copper. With citric acid present in slurry system, it plays a role of formation a native passivation film on the surface. The polishing rate of copper increases as the concentration of HNO3 increases or citric acid decreased. In H2O2 based slurry, H2O2 both dissolute of copper and form a cupreous oxide passivation surface. H2O2 is a strong oxidizer, it provides a potential to copper to be oxidized, maybe cupric ion or cuperous oxide simultaneously. For small amount of H2O2 adding in acidic region, it increase the dissolution the copper that increase the polishing rate of copper. With more H2O2 in slurry, the oxide film formation rate increases and the dissolution rate of copper decreases, as a result the CMP removal rate of copper film decreases. With Benzotriazole(BTA) present in HNO3 based slurry, BTA passivated the copper surface from HNO3. And the copper removal is conducted by the abrasive polishing off the BTA from the copper surface then etching the copper surface by HNO3. In this study, we wish to investigate the concentration of oxidizer and inhibitor effect in acidic slurry system on the polishing mechanism of copper CMP. Electrochemical impedance-spectroscopy (EIS) measurements were applied in order to obtain a better fundamental understanding of the electrochemical reaction and the physical model of copper in the CMP process.

MS-MoP4 Line Type SAC with Oxide Spacer(LSOS) Adopting Flowfill Oxide for 0.10µm Design Rule and Beyond*, **S.C. Park**, S.D. Lee, S.T. Ahn, J.C. Ku, D.S. Kim, J.W. Kim, H.K. Yoon,* Hynix Semiconductor, Inc., Korea

In this study, we used Flowfill oxide in the Line-type SAC with Oxide Spacer(LSOS) process, a storage node contact formation technology for DRAM devices. During our LSOS process, a bit-line sidewall was formed after SAC etching, which substantially reduced the aspect ratio of ILD gap-fill process.@footnote 1@ However, for 0.10µm design rule and beyond, even when the LSOS process was applied, small voids were created because conventional High Density Plasma(HDP) oxide was not able to fill the gap between bit-lines. Therefore, we selected Flowfill oxide as a novel InterLayer Dielectric(ILD) material instead of HDP oxide. The key attribute of Flowfill oxide is a unique chemistry of SiH@sub 4@ and H@sub 2@O@sub 2@, which generates a liquid-like intermediate compound that fills very narrow gaps and provides excellent planarity.@footnote 2@ In this experiment, to deposit the Flowfill oxide, TRYKON Planar 200 system was used. A higher Si@sub 3@N@sub 4@ selectivity was obtained when Flowfill oxide was used during the SAC etching, compared to HDP oxide. To find the exact cause of such a high selectivity with Flowfill oxide, X-ray Photoelectron Spectroscopy(XPS) was used to analyze partially etched Flowfill oxide and HDP oxide sample. The XPS analysis showed that a thicker fluorocarbon film was formed on Flowfill oxide and the carbon concentration of the fluorocarbon film was higher on Flowfill oxide. The difference of fluorocarbon film can be due to the presence of hydrogen in Flowfill oxide. In addition, we found that even though Flowfill oxide was annealed for the purpose of densification, nano-pores were created at the bottom of the gap between bit-lines. These nano-pores resulted in a partial stoppage of the SAC etching process, so we had to remove the remaining layer during the sidewall etching. Furthermore, we were able to check the practicality of the LSOS process with Flowfill oxide by fabricating a 256Mb density test vehicle having 0.10µm design rule. @FootnoteText@ @footnote 1@ K.H. Yoon, S.C. Park, et. al.,Symp. on VLSI Tech. Dig., 2001, in press. @footnote 2@ M. Matsuura, et. al., IEDM Tech. Dig., 1994, P.117

MS-MoP5 Application of Plasma V@sub dc@ Bias Diagnostics Cathode For Device Charging Damage Optimization*, **S. Ma**,* Applied Materials*; K. Horioka,* Applied Materials, Japan*; R. Lindley, K. Doan, S. Kats, M. Dahimene, Y. Xia, H. Shan,* Applied Materials

It is highly desirable to investigate the potential plasma damage issues as early as in the stage of plasma process chamber development without processing the real device wafers. Therefore a diagnostic tool is required to give reliable relationship to real device plasma damage and fast feedback on any process or hardware change. In this paper, a V@sub dc@ bias diagnostic cathode is used to measure the plasma induced self bias uniformity across the wafer and the correlation to device charging damage. A Magnetically Enhanced Reactive Ion Etching (MERIE) chamber is used to install this diagnostic cathode. Multiple probe pins are buried within the electrostatic chuck surface with only the top surface tips exposed to plasma. Wafer surface DC bias voltage during plasma process can be directly measured from these probes simultaneously with built-in circuitry. Real-time analysis of V@sub dc@ bias is thus feasible by multi-channel recording of bias evolution. The maximum bias difference (@delta@V@sub dc@ = V@sub dc(max)@ - V@sub dc(min)@) between the maximum and the minimum value of simultaneously measured V@sub dc@ across the cathode surface can be used to correlate to the potential driving voltage on the wafer to generate device damaging current during plasma process. Compared to real antenna MOS capacitor device damage data under similar process conditions, when @delta@V@sub dc@is less than a threshold around 12V then plasma induced charging damage is not a concern. This method also shows successful examples of different process recipes and hardware optimization to meet industrial device plasma damage spec.

Plasma Science
Room 134/135 - Session PS-MoP
Plasma Diagnostics and Plasma-Surface Interactions Poster Session

PS-MoP1 Molecular Structure of Fluorocarbon Deposits Analyzed by EIMS and CIMS Combined with Thermal Desorption Technique*, N. Takada,* ***K. Sasaki****, K. Shibagaki, K. Kadota,* Nagoya University, Japan

In order to understand plasma-surface interaction in fluorocarbon plasmas, the analysis of fluorocarbon deposits is an important issue. To date, x-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) are exclusively adopted for the analysis of fluorocarbon films. However, detail of the molecular structure of fluorocarbon films cannot be understood by XPS and FTIR. In the present work, we adopted electron-impact mass spectrometry (EIMS) and chemical ionization mass spectrometry (CIMS) for the analysis of the molecular structure of fluorocarbon films produced by C@sub 4@F@sub 8@ and C@sub 4@F@sub 8@-H@sub 2@ plasmas. A thermal desorption technique was used to evaporate fluorocarbon molecules from samples. In EIMS, thermally desorbed molecules were ionized by an electron beam with an energy of 70 eV. In CIMS, isobutene is ionized by electron impact to produce slow electrons. Negative fluorocarbon ions were produced via dissociative electron attachment of the slow electrons. The threshold temperature for thermal desorption of fluorocarbon molecules from a sample produced by a C@sub 4@F@sub 8@ plasma was 100-160 °C. Many peaks corresponding to mass numbers up to 800 were observed in the EIMS spectrum. The major peaks were classified into two groups having structures of CF@sub 3@(CF@sub 2@)@sub n@@super +@ and CF(CF@sub 2@)@sub m@@super +@. This result indicates that molecules desorbed from the sample contain the polymerized structure of CF@sub 2@. The overall shape of the CIMS spectrum of the fluorocarbon sample was similar to that of perfluorokerosene (PFK), which has a molecular structure of CF@sub 3@(CF@sub 2@)@sub n@CF@sub 3@. This suggests that fluorocarbon molecules desorbed from the sample have a molecular structure similar to PFK. By comparing the CIMS spectra of the sample and PFK, the mass number of the desorbed molecule was estimated to be 1100.

PS-MoP2 Real Time Analysis of the Remote Oxygen and Hydrogen Plasma Cleaning using Mass Spectroscopy*,* ***H. Soh****, H. Seo, Y. Kim, H. Jeon, Y.C. Kim,* Hanyang University, Korea

The plasma cleaning technologies have been attracting a great attention due to the demands of the compatible process with the most cluster tool and of the environmentally safe process. The photo resist (PR) ashing and PR strip processes are generally followed the silicon etching process to remove the PR and polymerized residues, respectively, during integrated circuit fabrication. However, the PR strip is the wet chemical process and causes environmental problems. Especially, the polymerized residues formed at the contact and via holes during the photo resist (PR) ashing and PR strip processes must be removed prior to the metal contact. In this study, we continuously monitored and systematically analyzed the volatile gases from the oxidized PR molecules during the low temperature remote plasma cleaning process. Mass spectroscopy (QMS200) was used for the real time monitoring of the volatile gases containing carbon and fluorine. In-situ Auger electron microscopy, X-ray photoelectron spectroscopy, atomic force microscope analysis systems were used to evaluate the cleaning effects and to avoid recontamination such as carbon absorption in the air. The surface morphologies of the samples before and after plasma cleaning were also observed using scanning electron microscope. This paper will present the oxygen and hydrogen remote plasma cleaning efficiency and its chemical reaction mechanisms. @FootnoteText@ @footnote 1@K.Sakuma, K.Machida, K.Kanoshida, Y.Sto, K.Imai and E.Arai, J.Vac.Sci. Technol.B 13(3), May/June (1995)

PS-MoP3 Investigation and Modeling of Plasma-Wall Interactions in Inductively Coupled Fluorocarbon Plasmas and the Effects of Chamber Dimension*,* ***E.A. Joseph****, S.P. Sant, L.J. Overzet, M. Goeckner,* University of Texas, Dallas*; M.J. Kushner,* University of Illinois, Urbana Champaign

Plasma-wall interactions in fluorocarbon based feedgas chemistries, namely CF4, are examined in both a standard and a modified inductively coupled Gaseous Electronics Conference (GEC) reference cell using In-Situ Fourier Transform Infrared Spectroscopy (FTIR). Initial measurements in the standard GEC reference cell show the dissociation of the CF4 feedgas into radical CFx species as has been observed elsewhere.@footnote 1@ Experimental results from both the standard GEC reference cell as well as the modified GEC reference cell, which differs from the standard cell in that it has easily configurable plasma exposed surfaces,@footnote 2@ are compared to results from the Hybrid Plasma Equipment Model@footnote 3@ to better elucidate the influence of the plasma exposed surfaces on plasma parameters including, but not limited to, plasma density, wall temperature, and CFx polymer thickness. @FootnoteText@ This material is based upon work supported by the National Science Foundation under Grant No. 0078669 @footnote 1@M. J. Goeckner, M. A. Henderson, J. A. Meyer, and R. A. Breun, J. Vac. Sci. Technol. A 12, 3120 (1994) @footnote 2@M. J. Goeckner, J. M. Marquis, B. J. Markham, and A. K. Jindal, Bull. Am. Phys. Soc. Vol. 45 No. 6 @footnote 3@R. Kinder and M. J. Kushner, J. Vac. Sci. Technol. A 19, 76 (2001).

PS-MoP4 Controllable Ion Source for Process Enhancement in a Downstream Plasma Ash Chamber*,* ***A.K. Srivastava****, P. Sakthivel, I. Berry,* Axcelis Technologies, Inc.*; H.H. Sawin,* Massachusetts Institute of Technology

Plasma ash tools have in the past been designed to generate a gentle downstream plasma impinging on the wafer. However, additional demands to remove residue, both in front-end and back-end processes have recently been imposed on these ash tools. This has led to a gradual transition of the old plasma asher into a ash-etch hybrid tool that can tolerate harsh etchants in moderate amounts, and also have the flexibility of controlling the ion flux to the wafer without charge damage. Different approaches have been attempted to meet these needs with limited success, mostly by taking the chamber towards the reactive ion etch (RIE) regime where the risk of device damage is high. A new approach to the dynamic control of ion generation and transport to the wafer, while maintaining operating regimes that are conducive to an ash tool and hence non-destructive to the wafer, is reported in this paper. In a typical downstream plasma ash tool, an upstream microwave discharge is fed into a plenum that disperses the reactive species through a hard-coated aluminum baffle plate above the wafer. When ion bombardment is required, a secondary ion source coupling radio frequency (RF) is switched on, creating a glow discharge in the plenum above the baffle plate. Under optimal conditions, electrons from the glow discharge are trapped inside the sheath of the baffle plate holes. These electrons complete the current path on the bottom surface of the baffle plate, and have sufficient energy to ionize some of the neutral gas. This secondary source of ions provides a gentle, low energy, uniform bombardment on the wafer. This paper describes the ion source in detail as it is used during specific ash/residue removal processes. The unique ion generation mechanism is discussed. Preliminary results of ion bombardment on the removal of the carbonized layer of implanted resist at low temperature are presented. Optical emissions data characterizing the ash chemistries are also presented.

PS-MoP5 A Multi-Technique Investigation of the Pulsed Plasma and Plasma Polymers of Acrylic Acid, Propanoic Acid and Hexamethylenedisiloxane*,* ***S. Fraser****, D. Barton,* University of Sheffield, England*; A.J. Roberts,* Kratos Analytical, England*; R.D. Short,* University of Sheffield, England, UK

The synthesis of thin plasma polymer films from radio frequency (rf) sustained glow discharges of small organic compounds is well documented.

Films containing a high degree of retention of the starting monomers original functionality and structure can be deposited using a low power plasma. These plasmas can be sustained by continuous wave (CW) or by pulsing a higher input power to achieve a lower average power. Plasma polymers of acrylic acid, propanoic acid and hexamethylenedisiloxane have been fabricated from pulsed 13.56 MHz RF plasmas in a "capicatively" coupled plasma deposition chamber. Plasma "on" and "off" (t@sub on/off@) times in the millisecond (ms) pulse time regime have been investigated using a peak plasma power of 50 W. Employing a fixed ton (5ms) the effect of toff (0-2000 ms) on the solid-phase plasma polymer has been investigated using X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF SIMS). Mass spectrometry has been employed to monitor the neutral and charged species in the plasma-gas as a function of toff and deposition rates have been monitored by means of a quartz crystal mass balance (QCMB). For comparison continuous (CW) wave plasmas of equivalent "average power" have been studied. The XPS (C1s core line) show that with increased t@sub off@ the extent of functional group retention increased. Valence band XPS and SIMS data indicate at low "average" powers (0.2 W) a linear polymer, closely resembling the conventional polymer, is deposited. The mass spectral data indicate the principal affect of t@sub off@ is on the amount of intact monomer in the system. For example, with acrylic acid this was shown by monitoring the signal from the molecular ion of acrylic acid (m/z 72) in the neutrals.

PS-MoP6 Synthesis and Characterization of New Material (BON) for Semiconductor Applications*, G.C. Chen, S.-B. Lee,* ***J.-H. Boo,*** Sungkyunkwan University, Korea

Recently, oxynitride compounds sparked among functional materials, such as Ti(ON), Si(ON) and SiBON. They presented a promising potential application of diffusion barrier, solar material and interlevel dielectric material. Since BON was declared as a by-product in synthesis of hard material, we have firstly developed the research on the molecular structure of new material (i. e. BON). In this study, we would like to report on the electrical property of BON thin films grown on Si(100) substrates by low frequency RF derived plasma assisted CVD. The effect of growth condition, such as flux of fed gas, deposition temperature as well as growth time, on the I-V characteristics are mainly discussed. The experimental results showed that the electrical resistance decreased with increasing the nitrogen flux and growth time. Amorphous BON thin film grown at relatively low temperature has more higher resistance than microcrystal containing thin film that obtained at high temperature, and the most smooth morphology was benefit of getting low resistance. By controlling nitrogen content in the film layer it can be possible to making the BON thin films that have either semiconducting or insulating properties. The as-grown new materials were characterized by XPS, RBS, FTIR, AFM, and TEM/TED. During CVD, moreover, the optical emission spectra (OES) were also measured in-situ for plasma diagnostics and analysing gas phase reaction. Based on the OES result, we confirmed that the formation of BON thin film was suit to be performed under nitrogen plasma.

PS-MoP7 The Effect of Controlling the Ion Energies of a Plasma Polymerised Deposition Surface Upon the Film Structure*,* ***D. Barton,*** *R.D. Short,* University of Sheffield, UK*; J.W. Bradley,* UMIST, UK, U.K.

The formation of plasma polymerised films has been the subject of intensive research over many years. Despite this work and the technological relevance of such films, little attention has been paid to the actual mechanisms involved in both the polymer formation and deposition. In particular, the question of whether the polymer is formed either in the bulk plasma, the sheath region, or at the surface remains unresolved. We present an experimental technique which allows the independent control of positive ion energies at a deposition surface. The technique relies upon feeding an RF signal to the surface which is matched in both phase and amplitude to the RF potentials in the plasma. In this way, it is possible to control the energy of the positive ions at the surface, independently of other plasma parameters. Ions may be a significant constituent of polymer films as previous measurements of the ion flux to a deposition surface have suggested that these particles may be responsible for about 25% of the total polymer mass. Embedded into the deposition surface are plasma diagnostics including a plasma mass spectrometer, quartz mass balance and an ion flux probe. The deposited films are analysed using XPS. Using an acrylic acid monomer, we will relate energy changes of ions striking the surface to the film properties such as extent of cross linking and functionality retention.

PS-MoP9 Uniformity Control of Electron Temperature and Density within a Commercial-scale Helicon Plasma Processing Reactor*,* ***M.J. Neumann,*** *J.E. Norman, D.N. Ruzic,* University of Illinois at Urbana

A study of electron temperature and density profiles was performed with PlasmaQuest 256 helicon plasma processing research reactor to better understand power absorption within a plasma reactor operating in helicon mode. The plasma source is a PMT Mori 200 antenna, coupled with an inner and outer opposing magnetic field coil placed around the it and a third coil positioned below it. The use of external magnetic field coils gives the ability to quickly change from one operating mode and condition to another. External electrical and magnetic variation effects are observed with a radially and z-varying Langmuir probes and spectroscopy. For nitrogen at 800 W RF and 80 A on the inner and lower magnets, the electron density profile was seen to decrease inward from 1.1x10@super 11@ cm@super -3@ at the edge of the chamber to 6.0x10@super 10@ cm@super -3@ in the center, while the electron temperature increased inward from 1.0 eV to 4.8 eV at the center of the chamber. In contrast, at 800 W RF and 40 A on the inner magnet alone, the electron density profile was seen to increase inward from 2.0x10@super 10@ cm@super -3@ at the edge of the chamber to a peak of 7.0x10@super 10@ cm@super -3@, while the electron temperature decreased inward from 4.0 eV to 2.6 eV at the center of the chamber. Through manipulation of electron density and temperature, the surface properties of various biopolymers can be changed, while leaving the underlying material unchanged. One observable change is a decrease in the water contact angle with common biopolymers, such as low-density polyethylene and high-density polyethylene. These changing plasma conditions have also been observed with argon and oxygen. Modeling has been performed to show the physical mechanisms involved in the electromagnetic energy transfer to the plasma. Thus, within the same reactor chamber and via only external manipulation, very distinct plasma conditions yielding different interaction properties can be produced.

PS-MoP10 Atomic-Order Plasma Nitridation of Ultrathin Silicon Dioxide Films*,* ***T. Seino,*** *T. Matsuura, J. Murota,* Tohoku University, Japan

Atomic-order nitridation of SiO@sub 2@ by a nitrogen plasma without substrate heating has been investigated using an ECR plasma apparatus. A 3nm-thick SiO@sub 2@ was thermally grown by wet oxidation of Si(100) at 700@super o@C. The SiO@sub 2@ film was nitrided by the nitrogen plasma for 1-324 min at the N@sub 2@ pressure of 1.3-2.6Pa with the microwave power of 200W. After plasma nitridation, some samples were annealed at 400-800@super o@C for 1hour in nitrogen. The depth profile was obtained by the repetition of etching by a 1%-diluted HF solution and XPS measurements. When the incident ions were exposed directly on the surface, the number of the incident ions (the product of the ion density and the plasma exposure time) was 3x10@super 15@-9x10@super 18@cm@super -2@, and the N1s peaks were observed at 397-398eV and at 402eV. With increasing nitrogen plasma exposure time, the N1s peak at 398eV shifted to 397eV corresponding to Si@sub 3@N@sub 4@. By annealing at 400-800@super o@C after nitridation, the N1s peak at 402eV disappeared. The depth profiles for the N1s peak at 397-398eV were almost the same before and after annealing. By a shutter placed above the wafer, the number of the incident ions was suppressed to 5x10@super 14@-1x10@super 16@cm@super -2@ and the ion energy (below 20eV) became lower than that (below 30eV) without the suppression of the incident ions, and the N1s peak was observed only at 399eV. By annealing at 600-800@super o@C after nitridation, the N atom concentration at 399eV was decreased due to the diffusion of the N atoms. This result is similar to the thermal nitridation of SiO@sub 2@ by NH@sub 3@. It is also found that the N atom concentration was normalized by the number of the incident ions in spite of the ion energy and the radical density. From these results, it is considered that the nitridation is caused mainly by the incident ions. It is suggested that the ion energy changes the binding conditions of N atoms in SiO@sub 2@.

PS-MoP11 Plasma Processing Tests from a Large Area High Density Plasma Source Based on Electron Beam Ionization*,* ***D. Leonhardt,*** Naval Research Laboratory*; S.G. Walton, D.D. Blackwell,* National Research Council*; D.P. Murphy, R.F. Fernsler, R.A. Meger,* Naval Research Laboratory

Electron beam ionization is both efficient at producing plasma and scalable to large area (square meters) when the electron beam is magnetically collimated. The beam ionization process is also fairly independent of gas composition, capable of producing low temperature plasma electrons (T@sub e@ ~ 0.5eV in molecular gases, 1-2eV in atomic gases) in high densities (n@sub e@ ~ 10@super 9@-10@super 12@ cm@super -3@).@footnote 1@ A 'Large Area Plasma Processing System' has been developed which consists of a planar plasma distribution generated by a sheet of 2-5kV electrons injected into a neutral gas background. The electron beam is magnetically collimated by a 150 Gauss field and operates in a gas pressures of 20-100 mtorr. A photoresist (PR) ashing process was studied under various system conditions In order to test plasma processing capabilities and control over processing parameters. The process system consisted of pure O@sub 2@ or O@sub 2@/Ar gas mixtures interacting with PR coated silicon substrates which were exposed to the plasma on an rf biasable (capacitively coupled) stage. Process conditions such as gas mixture composition, operating pressure, beam-to-substrate distance, duty cycle and incident ion energy were varied to determine the various effects of this plasma source on the PR ashing process. In situ Langmuir probe and mass spectrometry data@footnote 2@ are correlated to the material removal as determined by ex situ surface analysis (profilometry, SEM). Results show that the material removal process is ion energy dependent and highly anisotropic for ion energies @>=@50eV. Uniformity tests of the large area source will also be presented if time permits. Work Supported by the Office of Naval Research. @FootnoteText@ @footnote 1@D. Leonhardt, et al., AVS 47th Annual Symposium, Boston, MA, PS1-MoA5. @footnote 2@See presentation by S. G. Walton, et al., at this conference.

PS-MoP12 Energy Distributions of Ions and Neutrals from a Sputter Source*,* *G.J. Peter,* Inficon Limited, Principality of Liechtenstein, Liechtenstein*; N. Mueller, H. Zogg,* Inficon Limited, Principality of Liechtenstein

The kinetic energy of the deposited particles impinging on the surface of the substrate is an essential process parameter in sputter deposition processes. The energy as well as the mass of these particles can be measured with an energy selective mass spectrometer. Ions from the plasma can directly and easily be guided by an Ion Transfer Optics into the energy and mass filter resulting in a high sensitivity. In contrast to this, neutral particles have to be ionised first, before any energy or mass filtering can be done. It is common to use electron impact ion sources with well defined electrical potentials for ionisation, although this is a low efficiency process. For optimisation of the sensitivity for neutral particles, a wide acceptance angle of the ion is mandatory. This can be obtained by minimising the distance between the entrance aperture and the ion source. But this design is in no way optimum for the detection of ions, as at least the ion formation chamber of the ion source is a poor ion optics. So any design of a combined instrument will result in a poor sensitivity for the ions and a high sensitivity for the neutrals and vice versa. In order to overcome these difficulties, an otherwise standard plasma process monitor PPM 422 was equipped with two exchangeable, electrically insulated entrance apertures. One of it was used for the measurement of ions and the other one for detection of neutrals. The electrical insulation allows to set the aperture to any electrical potential. So a realistic simulation of the potentials on the substrate ca be performed. The energy distributions of particles from a gun type planar magnetron were measured with this modified device.

PS-MoP13 Species Characterization in Inductively Driven Fluorocarbon Etch Plasmas*,* *G.A. Hebner,* Sandia National Laboratories, usa*; I.C. Abraham,* Sandia National Laboratories

A number of techniques have been used to characterize etching plasmas containing fluorocarbon gases. Laser induced fluorescence was used to measure the spatially resolved SiF and SiF@sub 2@ densities in inductively driven discharges containing C@sub 2@F@sub 6@ and C@sub 4@F@sub 8@. Measurements of the spatially resolved SiF and SiF@sub 2@ densities were performed as functions of the induction coil power, pressure, and bias power above a silicon surface. The SiF density had a maximum at a radial distance of 2 - 3 cm from the center of the plasma, and then monotonically decreased towards the edge of the plasma region. The SiF@sub 2@ density had a maximum at a radial distance of approximately 7 cm from the center of the plasma. Electron and negative ion densities was measured in C@sub 4@F@sub 8@ and the identity of the negative ions in C@sub 2@F@sub 6@, CHF@sub 3@ and C@sub 4@F@sub 8@ containing discharges was investigated using a novel photodetachment experiment. To investigate the influence of surface material, the rf biased electrode was covered with a silicon wafer or a fused silica (SiO@sub 2@) wafer. In most cases, the trends in the electron and negative ion density were independent of the wafer material. A novel microwave resonant cavity structure was developed to identify the negative ions using laser photodetachment spectroscopy. Unlike traditional microwave cavity techniques, this method offers the possibility of spatial resolution. This work was supported by SEMATECH and the United States Department of Energy (DE-AC04-94AL85000).

PS-MoP14 Investigation on the Plasma Uniformity in Reactive Gas ECR Plasmas*,* *M. Shindo,* *Y. Kawai,* Kyushu University, Japan

Reactive gas plasmas are widely used in etching process for fabricating ULSI. In order to reduce the production costs, a uniform and high-density plasma with a large diameter is required. An ECR plasma can be a candidate for such a plasma, since it easily reaches more than 10@super 12@cm@super -3@. In addition, one of the mechanism of the uniformity in an Ar ECR plasma was clarified by Ueda and Kawai.@footnote 1@ On the other hand, the transportation and diffusion mechanism in reactive gas plasmas become complicated since a large quantity of negative ions are produced. Thus, it is necessary to investigate the plasma uniformity under the existence of much negative ions. In this study, an attempt to measure the spatial distribution of charged species in O@sub 2@/Ar and C@sub 4@F@sub 8@/Ar ECR plasmas was made. Here, the density of negative ions was estimated from the phase velocity of the ion acoustic waves (fast mode) which were launched from a wire antenna to which the positive pulse voltages (30µ sec in duration time and V@sub pp@=40V) were applied, and were detected with a plane Langmuir probe biased at -90V. The detected signals were observed with an oscilloscope, and a trough and a crest were found, corresponding to the waves excited at the leading and falling edge, respectively. As a result, the negative ions existed near the wall rather than the center region. Moreover, it was found that the positive ion density was uniform in the center region, and the uniform area widened as the reactive gas mixture rate was increased. @FootnoteText@ @footnote 1@Y. Ueda and Y. Kawai, Appl. Phys. Lett.71 (1997) 2100.

PS-MoP16 A Novel Approach to Time Resolved Langmuir Probe Measurements*,* *A.K. Jindal,* *S.K. Kanakasabapathy, M. Goeckner, L.J. Overzet,* University of Texas at Dallas

Langmuir Probes, when used carefully, have provided spatially resolved plasma density, potential, and electron temperature measurements. However, time resolved Langmuir Probe measurements are time consuming in triggered box car averaged systems. We present a novel approach to time resolved Langmuir Probe I-V curve acquisition. Probe Current and voltage are measured as functions of time, for a fixed applied DC bias, with a digitizing oscilloscope. These traces are collected and a new applied bias is set. By doing this repeatedly, we build up I-V-t profiles. Then, in an offline fashion, time is eliminated between these various traces and I-V curves are obtained for all instances of time in the pulse period. In contrast to state of the art triggered box car averaged systems, I-V curves are obtained with better time resolution and much faster. For example: I-V curves for 512 instances of time within a 1 msec pulse period with 300 points in voltage, is obtained in as little as 15 minutes. Once these time resolved I-V curves are obtained, appropriate probe theory is used for extracting time resolved plasma parameters using a Levenberg-Marquardt@footnote 1@ fitting algorithm. The high speed of data acquisition minimizes the effects of long-term plasma drift associated with slower techniques. We shall be presenting data from pulsed Chlorine and Argon discharges using this technique. . @FootnoteText@ @footnote 1@W.H. Press, S.A. Teukolsky, W.T. Vetterling, and B.P. Flannery. NUMERICAL RECIPIES in C: The Art of Scientific Computing. Cambridge University Press. .

PS-MoP17 Evaluation of Langmuir Probe Theories via Comparison with Microwave Interferometry and Plasma Oscillation Probe Methods in ICPs*,* *J.D. Evans,* *F.F. Chen,* University of California, Los Angeles*; W. Zawalski,* Hiden Analytical, Ltd., England

Measurements of plasma density (Np) are performed under identical conditions using microwave interferometry (MWI), plasma oscillation probe (POP) and Langmuir probes. Np via MWI is treated as the "known" result to which the other techniques are compared. Data is obtained in a chamber that lies downstream from a PlasmaTherm ICP source, over a wide range of parameters: Prf<1kW, Te=2-5eV, Np=10^10 - 10^12 cm^-3. Ne obtained via POP agrees well with MWI in relatively low-collisional regimes, as expected. I-V curves are acquired using Hiden Analytical's ESPion Langmuir probe, which employs broadband RF compensation via inline chokes and a compensation electrode. A variety of probe tip radii are used, which allows for a broad base of comparison. Conventional probe theories (OML, ABR and BRL) are used, as well as an approximation based on the assumption that the ion current (Ii) is determined mainly by the unipolar sheath expansion, whose thickness follows a modified Child-Langmuir (C-L-mod) law in which Ii is nearly proportional to Vo^(4/3), where Vo = |Vbias-Vplasma|. Different probe theories yield vastly differing values of ion density (Ni), whereas Te is reliably determined in most cases. In most cases the dependence of Ii with Vo agrees very well the C-L-mod law. Excellent agreement between Ni thus obtained and the MWI results is observed throughout the parameter range. However, it is also found that Hiden's ESPsoft algorithm, which employs OML theory that predicts Ii^2 proportional to Vo, yields values for Ne in good agreement with those of MWI and POP. Reasons for the success of the C-L-mod law in light of this apparent paradox are presented.

PS-MoP18 Electron Energy Control in an Inductively Coupled Plasma by Means of Induction Field Reversal*, H. Shindo,* *Tokai University, Japan; T. Urayama,* ADTEC Plasma Technology CO., LTD, Japan*; Y. Horiike,* The University of Tokyo, Japan*; S. Fujii,* ADTEC Plasma Technology CO., LTD, Japan

In the deep submicron etching for ultra large-scale-integrated circuit (ULSI) processes, the development of low-pressure and high density plasma sources has been highly required. In these plasmas, however, several crucial problems have risen up in conjunction with electron energy. These are related to the fact that the electrons are prone to be excessively energetic in high density plasmas generated at low pressures. In this work, we studied electron energy control in an inductively coupled plasma by employing different azimuthal mode antenna. It is expected for electron energy to reduce at higher azimuthal mode antenna, because induction field is reversed with a shorter length. The experiments were carried out in an inductively coupled plasma (ICP) which was produced in a stainless-steel chamber of 350 mm in diameter by supplying the RF power of 13.56 MHz through the quartz window at one end. The three types of antenna were prepared.The electron temperature could be reduced by increasing the azimuthal mode number of one-turn antenna with no notable change in electron density. These effects were remarkable in low pressures below 10 mTorr, hence in a condition of longer electron mean free path. The mechanism for these behaviors is that the electron temperature at lower pressures depends on both the electron mean free path and the field reverse distance, as anticipated. The electron gains more energy with larger field reverse distance so long as the mean free path is same, and the electron mean free path is inversely proportional to the pressure.The RF magnetic field was also measured by a pick up coil, and its behavior was quite consistent with the electron energy, meaning that the electron energy change is not due to the capacitive effect. It was concluded that the induction field reverse distance in conjunction with electron free path was essential in electron energy control.

PS-MoP21 Novel In Situ Diagnostics for Plasma Processing of Advanced Materials*, E.A. Evans,* ***G. Zhang****,* University of Akron*; A. Salifu,* Cree Research

Kinetic and transport parameters for nitride growth and processing are required for process design and optimization. A new approach for accurately determining these parameters at processing conditions will be presented. We have combined a large inductively coupled plasma reactor with a digital microbalance to make measurements of substrate weight during plasma processing of aluminum and aluminum nitride samples. The current set-up is capable of sensing growth and/or etch rates on the order of 1 microgram per second regardless of substrate area. We will present results that demonstrate the usefulness of these measurements for understanding the kinetic and transport mechanisms involved during plasma processing. These relationships are important not only for controlling oxidation during and after deposition but also for identifying growth regimes for high quality thin film nitride materials.

PS-MoP22 Analysis of Chlorine-Containing Plasmas*,* ***G.F. Franz****,* Infineon Corp., Germany

Capacitively coupled discharges of strongly reactive atmospheres containing mixtures of boron trichloride and chlorine are investigated employing impedance measurements, Langmuir probe measurements, optical emission spectroscopy (OES), and self-excited electron resonance spectroscopy (SEERS). The analysis covers the whole area spanned by these gases (including some mixtures), discharge pressure and RF power over more than one order of magnitude, and their impact on important plasma parameters like plasma density, plasma potential, electron temperature, temperature of the plasma bulk, electron collision rate with neutrals, and actual RF power coupled into the discharge. From these, other properties (electrical conductivity, capacitance, plasma bulk resistance, sheath resistance and its thickness) can be derived. Since the methods are partially complementary, a mutual control of the obtained data is made possible, and the limits of the methods can be evaluated. Compared to discharges of inert gases, which are used as calibration standard, electron plasma density and electron temperature are both definitely lower, which is mainly caused by electron attachment of the electronegative molecules. Absolutely no chlorine ions could be found in the plasma which is referred rather to the effective cooling of the Cl-containing species than to the nonexistence of these species. Furthermore, we compared values for the electron temperature and the plasma density obtained with OES and SEERS, respectively, and with the Langmuir-probe system. The concordance in both properties is surprisingly good, despite the fact that the electron energy distribution should be described with two temperatures and only Langmuir is spatially resolved. The variation of the calculated dc conductivity either from impedance measurements or combined Langmuir/SEERS lies within a factor of 2 and is mainly referred to uncertainties of the current path rather than to principal faults of the various methods.

PS-MoP23 Fluorocarbon Decomposition Products and Effluent Analysis from Atmospheric Pressure Dielectric Barrier Discharges*,* ***S.F. Miralai****, S. Mukhopadhyay,* Wright State University*; V. Shanov,* University of Cincinnati*; S. Datta,* Procter & Gamble

Dielectric barrier discharges (DBDs) are gaining increased attention as an economical and reliable method for generating non-equilibrium plasma conditions in atmospheric pressure gases. This has led to a number of important applications including industrial ozone generation, surface modification of polymers, excitation of CO2 lasers and large area plasma flat panel displays. One of the challenges in the development of applications of DBD is an understanding of reactive species generated in the plasma and analysis of effluent gases. Some of the reaction products in the effluent gases are in very low concentration, increasing the complexity of the detection process. This paper deals with the detection of reactive species and products in the plasma and in the effluent gases from a fluorocarbon dielectric barrier discharge plasma . Dissociation efficiencies of fluorocarbons at various frequencies and using different carrier gases , such as helium, nitrogen, argon and oxygen will be presented. Analysis of the reactive species and products will be described, using Optical Emissions Spectroscopy (OES) and Quadrupole Mass Spectrometry. Correlation of experimental data with preliminary modeling results will be presented.

PS-MoP24 Endpoint Detector for Controlling Clean and Passivation in HDP-CVD Processes*,* ***R. Rulkens****,* Novellus Systems, Inc.

Optical Emission Spectroscopy was used to develop a sophisticated End Point Detector for the clean and passivation steps of HDP CVD processes. During the clean process steps, NF3 plasma removes build-up of SiO2 on the reactor walls. The end point detector in real time determines the optimal time at which the silica film is removed from the reactor walls and prevents over or under etching. After the clean steps, a Hydrogen plasma is used in the passivation step to remove residual fluorine. In a similar manner, the End Point Detector determines the optimal time needed for passivation. The diagnostics are incorporated into the equipment hard- and software and automatically control the correct timing of the clean and passivation steps.

Surface Engineering
Room 134/135 - Session SE-MoP
Poster Session

SE-MoP1 Developments in Ammonium-based Solution with Inhibitors and Ionic Carboxylic Acids on Post Cu CMP Cleaning for Removal Colloidal Silica Abrasives*, S.-Y. Chiu,* ***T.-C. Wang****, Y.-L. Wang,* National Chiao Tung University, Taiwan, R.O.C.*; M.-S. Tasi,* National Nano Device Laboratories, Taiwan, R.O.C.*; M.-S. Feng,* National Chiao Tung University, Taiwan, R.O.C.

During the Cu CMP process with colloidal silica based slurry, colloidal slica abrasives would be selectively adsorbed onto copper line. These particle defects will influence the yields of the folloing thin deposition and lithography process. In this study, an approache are proposed to overcome the corrosion problem of copper line and to remove chemisorbed colloidal silica from polished copper surface. The clean solution would be formulated by adding ionic carboxylic acids into ammonium-based solution with inhibitors. We also elucidated the influence of electrostatic interaction between colloidal silica abrasives, copper and silicon dioxide films. Electrochemical polarizatio, zeta potetial, contact angle, AFM, SEM, surface scan, KLA defect mapping, and electro-property analyses are being evaluated for monitoring silicon dioxide (the polish stop layer) and copper films during post Cu CMP cleaning process. By means of these analytical methods, an suitable post Cu CMP cleaning chemistry in alkaline ammonium-based solution with inhibitor and carboxylic acids was developed to effectively remove colloidal abrasives left on the wafer, meanwhile not to cause copper wires corrosion.

SE-MoP2 Mechanical Properties of Polymer-carbon Nanotube Composite*, **C. Wei**, K. Cho,* Stanford University*; D. Srivastava,* NASA Ames Research Center

Recently carbon nanotubes are considered as nanoscale fibers which can strengthen polymer composite materials. Nanotube-polymer composite materials can be used for micron scale devices with designed mechanical properties and smart polymer coating to protect materials under extreme physical conditions. To explore these possibilities it is important to develop a detailed atomic scale understanding of the mechanical coupling between polymer matrix and embedded nanotubes. In this work we study the mechanical properties of polymer-carbon nanotubes (CNT) composite using molecular dynamics (MD). We will discuss the contribution of Van der Waals potential to the load transfer from matrix to nanotube. Our MD simulations show that polymer can chemically bonded to CNT. We will discuss about the resulting mechanical coupling between the CNTs and polymer matrix to develop an efficient nano-composite materials.

SE-MoP4 Effect of Pre and Post Surface Modification on Copper (II) Fluoride Formation in the Cu/PTFE System*, **J. Torres**,* Johns Hopkins University, US*; C.C. Perry, S.R. Carlo, D.H. Fairbrother,* Johns Hopkins University

Fluoropolymers are attractive materials for devices in the microelectronics industry because of their desirable physical, chemical, and dielectric properties. Copper is best suited for interconnect wiring because of its low resistivity and electro-migration; unfortunately, its adhesion to fluoropolymers is generally poor. In this study we present results of the effect of Ar@super +@ and X-ray pre and post treatment of PTFE surface in terms of CuF@sub 2@ formation. There seems to be correlation between adhesion and chemical reactivity with the surface, thus, any pre or post processes that initiate the formation of Cu-F bonds will enhance adhesion. Although there are studies in the literature that characterize the Cu/PTFE interface, few studies have concentrated specifically on pre- and post surface modification with respect to compound formation. Copper thermally evaporated on unmodified PTFE is chemically inert, forming a metallic overlayer; no Cu-F bond formation in either the F(1s) or C(2p) XPS regions was observed. Pretreatment of PTFE with either Ar@super +@ or X-ray irradiation was found to be ineffective in activating the surface towards Cu-F bond formation during physical vapor deposition of Cu. In contrast, post-surface modification of the Cu/PTFE interface with either Ar@super +@ or X-ray irradiation resulted in the production of CuF@sub 2@. The extent of CuF@sub 2@ production was found to be similar for both Ar@super +@ and X-ray irradiation post-treatment strategies for comparable initial Cu coverages, suggesting a common reaction mechanism for the formation of CuF@sub 2@. AFM images of virgin PTFE show an amorphous surface, composed of globular features, while after Ar@super +@ treatment the surface becomes fibrous. When Cu is deposited on PTFE the surfaces appearance is smooth as a result of the metallic overlayer.

SE-MoP6 Adhesion Enhancement of Thin Film Metals onto Polyimide Substrates by Bias Sputtering*, S.Y. Kim, J.S. Kang, **Y.H. Kim**,* Hanyang University, Korea

The adhesion of thin film metals deposited by bias sputtering has been studied. Al, Cr, Ta, and Ti thin films have been deposited onto polyimide substrates using DC magnetron sputter. RF bias of 0 ~ 400 watt was applied to the substrate during DC sputtering. The adhesion was evaluated using a 90 degree peel test. The peel adhesion strength was low when the RF bias was not applied during sputtering. However, it increased with RF bias power in all specimens. Scanning electron microscopy and Auger depth profile indicated that polyimide cohesive failure occurred during peeling and heavy deformation was observed in the metal films peeled from polyimide substrates when RF bias was applied during deposition. Cross-sectional transmission electron microscopy showed the thin implanted layer of metals in the polyimide interface. The implantation layer was likely formed due to the RF bias to the substrate. This implantation effect can explain the adhesion enhancement by bias sputtering.

SE-MoP7 Oxidation Properties of Zn and Ni-Zn co-deposited with Nanometer Diamond Powder*, **W.-H. Lee**,* National Taipei University of Technology, Taiwan, ROC

The co-deposition of nickel and zinc with or without reinforcement of nanometer diamond powder were successfully manufactured by the method of electro-plating process on the carbon steel substrate. The variables investigated within this research work include the additions of ZnCl2, anode current density (ACD) and cathode current density (CCD), PH value, plating temperature, and the concentration of nanodiamond powder in nickel sulphamate plating solution. It revealed that g (Zn21Ni5) phase could be plated on the specimen surface with the thickness of 30 ¢Ggm for 1 hour plating time. The diamond powder used in this research work had an average size of 25 nm and concentration of 2 g/l to 20 g/l in the solution. After experiments, the corrosion resistance of these co-deposited plating layers was tested by the salt spray (fog) testing procedure for 0.5 to 30 days. It was found that the pure Ni-Zn alloy without co-deposited with nanometer diamond powder exhibited three times of corrosion resistance than that of with reinforcement of nanodiamond powder. The structure, surface morphology and the cross section of plating layers were examined by the x-ray, SEM, and optical microscope. The distribution of chemical compositions of plating layers was analyzed by the energy despersive analyzer of x-ray (EDAX) as well.

SE-MoP8 The Effect of Cooling Conditions on Plasma-Carbonitrided Iron Surfaces*, L.C. Gontijo, R. Machado, E.J. Miola,* Universidade Federal de Sao Carlos, Brazil*; L.C. Casteletti,* Universidade de Sao Paulo, Brazil*; **P.A.P. Nascente**,* Universidade Federal de Sao Carlos, Brazil

Plasma- carbonitriding has been used to improve the tribological and mechanical properties of materials, specially iron-based alloys. In this work, the Pulsed Glow Discharge (PGD) technique was employed for carbonitriding pure iron. This method is more economical than others because it provides for faster nitrogen and carbon diffusion, which in turn allows for lower processing temperatures and shorter treatment times with satisfactory results. Three sample sets were carbonitrided in a gas mixture of 2 vol. % CH@sub 4@, 20 vol. % N@sub 2@, 78 vol. % H@sub 2@, under a pressure of 400 Pa, discharge frequency of 9 kHz, temperature of 580 °C, during 90 minutes. The first sample set was cooled under vacuum, the second set, under air, and the third set was quickly removed from the furnace and then quenched in oil. The three sample sets were characterized by optical microscopy (OM), scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). For the samples cooled under vacuum, the diffusion zone comprised of enlongated needle-like precipitates and shorter ones, which were identified as @gamma@'-Fe@sub 4@N and @alpha@"-Fe@sub 16@N@sub 2@, respectively. The same phases were also observed in the diffusion zone of the samples cooled under air. However, these phases were not detected in the samples quenched in oil. The compound layer for the three sample sets consisted of @gamma@'-Fe@sub 4@N and @epsilon@-Fe@sub x@(N,C). An austenite (@gamma@) transformed zone was detected in between the compound layer and the diffusion zone.

SE-MoP9 The Temperature Effects on Surface Energy of PVD Coatings*, **S.M. Chiu**,* Metal Industries R&D Centre, Taiwan, ROC, Taiwan*; T.P. Cho, C.W. Chu,* Metal Industries R&D Centre, Taiwan, ROC*; Y.-C. Chen,* Shu-Te University, Taiwan, ROC

There are serious sticking and wear problems in the molds surface during the IC packaging and die casting processes while the operation temperature ranges from 150°C to 800°C.Some surface treatment are performed on high speed steel for comparing the surface energy properties in different temperature and atmosphere condition.The surface energy properties was studied by the contact angle measurement.The surface treatments include electroplated hard Cr,PVD Cr-based and DLC coatings. The films microstructure is examinated by atomic force microscopy,SEM and X-ray defraction .The control of the surface morphology and phase structure of the coatings is most important to obtain low surface energy properties.

SE-MoP10 Effect of Heat Treatment on the Oxidation and Properties of Ion-Plated ZrN Thin Film on 304 Stainless Steel*, **W.-J. Chou**,* National Tsing Hua University, ROC, Taiwan*; G.-P. Yu,* National Tsing Hua University, ROC*; J.-H. Huang,* National Tsing Hua University, ROC, Taiwan

It is a common practice to apply heat treatment processes for improving the structure and properties of thin films. One of the problems during heat treatment process is the contamination and oxidation of the thin film by the atmosphere in the furnace. To solve the problem, using a controlling atmosphere in the furnace, especially lowering down the oxygen partial pressure, is considered to be the most effective method. In this study, an oxygen meter was used to monitor the furnace atmosphere during the heat treatment process, and the oxygen partially pressure was controlled down to 10-15 atm. Zirconium nitride (ZrN) films deposited on 304 stainless steel, by a hollow cathode discharge ion-plating (HCD-IP) technique, was used as the specimen in heat treatment. The thickness and composition of the coated specimen were controlled to be 0.6 mm and N/Zr=1, respectively. The residual stress and preferred orientations of the ZrN films were determined using X-ray diffraction (XRD). Hardness of the films was measured by nanoindentation. Atomic force microscopy (AFM) was used to study the surface roughness of thin film. The extent of surface oxidation and composition of the ZrN film were determined using X-ray photoelectron spectrometry (XPS). The (111) texture coefficient increases with increasing treatment temperature. The hardness of the ZrN film was rapidly increased after heat treatment. The oxidation of the thin film was incapable avoided even in the gas atmosphere with an oxygen partially pressure lower than 10-15 atm.

SE-MoP11 Deposition of Ti(C,N) and Zr(C,N) Thin Films by Plasma Assisted MOCVD and In-situ Plasma Diagnostics with Optical Emission Spectroscopy*, Y.K. Cho, J.S. Yoon,* ***C.-H. Heo****, J.G. Han, S.W. Lee, J.-H. Boo,* Sungkyunkwan University, Korea

Ti(C,N), Zr(C,N) films are synthesized by pulsed D.C. plasma assisted metalorganic chemical vapor deposition (PA-MOCVD) using metal-organic compounds of tetrakis diethylamido titanium and tetrakis diethylamido zirconium at 200 °C to 300 °C. H@sub 2@ and He+H@sub 2@ gases are used as carrier gases to compare plasma parameter. The effect of N@sub 2@ and NH@sub 3@ gases as reactive gas is also evaluated in reduction of C content of the films. Radical formation and ionization behaviors in plasma are analyzed by optical emission spectroscopy (OES) at various pulsed bias and gases conditions. He and H@sub 2@ mixture as carrier gas is very effective in enhancing ionization of radicals, especially N@sub 2@ resulting is high hardness. However, NH@sub 3@ as reactive gas highly reduces formation of CN radical, there by decreasing C content of Ti(C,N) and Zr(C,N) films in a great deal. The hardness of film is obtained to be 1400 HK to 1700 HK depending on gas species used and bias voltage. Higher hardness can be obtained for H@sub 2@ and N@sub 2@ gas atmosphere and bias voltage of 600 V. Plasma surface cleaning using N@sub 2@ gas prior to deposition appear to increases adhesion of films on cold forming steel. The changes of plasma including radicals and film properties are illustrated in terms of carrier and reactive gases as well as pulsed power variation.

SE-MoP12 A Study of Nitrided Layers of SAE 303 Stainless Steel using a Magnetized Plasma Process*, G.A. Lacerda,* Instituto Tecnologico de Aeronautica - ITA - Brazil, Brazil*; C. Otani,* ***H.S. Maciel,*** Instituto Tecnologico de Aeronautica - ITA - Brazil*; C. Alves Jr.,* Universidade Federal do Rio Grande do Norte, Brazil

Iron nitride is an important material in metallurgy, especially as constituent of the so-called compound layers generated on the surface of workpieces made of steel and hardened by nitriding and carbonitriding. More recently the iron nitrides reappeared in the literature but now as thin films and as potencial candidates for magnetic recording heads or eventually recording media. Dealing with an investigation of this subject, a series of plasma nitriding experiments has been conducted on SAE 303 austenitic stainless steel samples, using an experimental system based on an ordinary dc glow discharge which was located between the magnetic poles of an electromagnet. In this system the sample is placed on the cathode and the magnetic field (B), which is uniform and perpendicular to the sample surface, can be varied from zero to 1440 Gauss. The nitriding processes were carried out under constant substrate temperature of 430 °C and gas pressure of 5.0 Torr, whereas different N@sub 2@-H@sub 2@ gas mixtures were used. The nitrided layers were characterized by micro-hardness testings, X-ray diffraction, conversion electron Mössbauer spectroscopy and scanning electron microscopy. The results showed a strong influence of the applied magnetic field upon the mechanical properties of the samples surface as consequence of different nitride phase growing. A decrease in the surface hardness with the increase of the magnetic field strengh was observed for all the conditions tested. For certain gas mixtures, as for example 50%N@sub 2@-50%H@sub 2@, a noticeable effect occurred, i.e., at low and high B field, in the range provided by the electromagnet, the prevalent structure of the nitrided layer is dominated by the Fe@sub 3@N, but it changes to Fe@sub 4@N based structure for B field in the middle range of (260-770) Gauss.

SE-MoP14 Microscopic Polishing of Cu Thin Films using Atomic Force Microscopy*, K.M. Fishbeck, M.D. Arthur, J.S. McDonald, K.L. Muessig, D.C. Koeck,* ***H.C. Galloway****,* Southwest Texas State University*; M.-S. Lim, S.S. Perry,* University of Houston

Chemical Mechanical Planarization of microelectronic wafers in multiple stages of fabrication is an important process in creating efficient multilayer devices in the modern semiconductor industry. The CMP process uses a rotating pad to apply pressure to a wafer surface exposed to a polishing slurry composed of both a corrosive solution and suspended abrasive particles. In order to study the fundamental mechanisms of CMP, an Atomic Force Microscope is used in conjunction with a liquid cell to simulate the CMP process. Copper thin films grown on Si wafers are exposed to chemicals of variable composition in the liquid cell, with the force of the AFM tip itself providing the mechanical component of the CMP process. A sputtering process is used to coat the AFM cantilever tips with a thin film of alumina to more closely model a single abrasive particle in a CMP slurry. The solutions used in the liquid cell are of varied concentrations and consist of both a corrosive agent(HNO@sub 3@ or NH@sub 4@OH) and a suitable corrosion inhibitor. The materials used for both the samples and the tip coating were chosen for their relevance to current microelectronic fabrication applications, as were the solution components used in the liquid cell. In this way it is possible to study the localized effects of CMP on the exposed samples as a functions of force, solution chemistry, and exposure time. In situ AFM imaging at varying time intervals allows analysis of both material removal processes and surface topography changes.

Surface Science

Room 134/135 - Session SS1-MoP

Electronic Structure Poster Session

SS1-MoP1 The Surface Sensitivity of the Unoccupied Bands of Mo(112)*,* ***H.-K. Jeong****, T. Komesu,* University of Nebraska-Lincoln*; I.N. Yakovkin,* National Academy of Sciences of Ukraine*; P.A. Dowben,* University of Nebraska-Lincoln

We present results of unoccupied states of Inverse photoemission on Mo (112). The data are compared with the calculated band structure. The comparison between the calculated and experimental bands along the of the surface Brillouin zone is key to the elucidation of the important features of the electronic structure of Mo (112) surface. Because the Brillouin zone does not change along for these two surfaces, the angle - resolved inverse photoemission spectra can be compared to determine surface sensitivity all along this symmetry direction from zone center to zone edge. Enhanced surface sensitivity of inverse photoemission from the comparison of spectra for clean and the p(1x2) oxygen covered surfaces has been investigated. In particular, different sensitivity of the surface states 0.5 eV and 2.2 eV to oxygen adsorption can be attributed to different symmetry of the states at the surface Brillouin zone center. Thus, the 0.5 eV state found to have a1 symmetry in theory, while the 2.2 eV band is found to be odd with respect to the mirror plane in theory.

SS1-MoP3 High Spatial Resolution Soft X-ray Photoemission Study of WO3 Thin Films*,* ***L. Lozzi****, M. Passacantando, S. Santucci,* University of L'Aquila, Italy*; S. La Rosa, N. Yu Svetchnikov,* Sincrotrone Trieste SCpa, Italy

Tungsten trioxide (WO3) is a wide gap n-type semiconductor and it is the subject of an intense both theoretical and experimental studies because of its interesting applications, such as gas sensors towards different gases, like NO2 and H2S, and as electrochromic film. Many of these possible applications are mainly due to the oxygen vacancies. For example, in the sensing mechanism, the gas species are adsorbed on the surface changing the concentration of the free electrons on the surface. These electrons are present on the surface because of the oxygen vacancies. The variation of this concentration modifies the electrical conductivity of the film. Similarly, the presence of substoichiometric WO3-x compounds, determines the optical properties of these films. An important parameter in the preparation of WO3 thin films is the thermal treatment following the sample growth. For example it has been shown that the gas sensitivity and response time are strongly influenced by the annealing procedure, because of the phase transitions induced by the annealing. In this work the WO3 surface chemical composition has been studied by means of high resolution soft X-ray photoemission spectroscopy. We have studied the surface properties of both as deposited samples and samples after annealing in air at high temperatures. Valence band and W 4f core levels have been analysed on different samples positions and high resolution maps have been acquired. The valence band spectra have shown W 5d density of state at the Fermi level, indicating the presence of metallic tungsten on the surface. This has been confirmed by the W 4f signal, which present both metallic and oxidized phases. The high resolution maps, obtained following both valence and core states, have clearly evidenced the presence non stoichiometric areas and of some metallic islands.

SS1-MoP4 Femtosecond Dynamics of Electrons in Image-potential States on Stepped Cu(001)*, **M. Roth**, M. Pickel, J. Wang, M. Weinelt, Th. Fauster,* Universität Erlangen-Nürnberg, Germany

The Rydberg-like series of image-potential states (|n>, n = 1, 2, ...) is a prototype system for loosely bound electrons at a metal surface. The electronic structure and the femtosecond dynamic of these states is studied by energy- and time-resolved two-photon photoemission spectroscopy. The electron trapped in the image-potential moves virtually free lateral to the surface exhibiting a parabolic dispersion with effective mass close to the free-electron mass. In this intermediate state the electron is subject to inelastic and quasielastic scattering processes which cause decay of the population and phase relaxation. The influence of surface corrugation on these processes has been investigated for stepped Cu(117) and Cu(119) surfaces which are vicinal to Cu(001). The dynamics depend on both the distance of the electron in front of the surface (~ n@super 2@) and the parallel momentum perpendicular to the step edge. Only for the lowest image-potential state |1> we can identify umklapp processes. An electron in this state which moves upstairs apparently has a longer lifetime than an electron moving downstairs. In the second image-potential state |2> the decay rate decreases linearly with kinetic energy but independent of direction. While quasielastic scattering with small momentum transfer is mainly observed for the first image-potential state, the population of state |2> decays in addition via resonant scattering from the band bottom to states of band |1> with finite momentum. Compared to the Cu(001) surface the latter process is considerably enhanced on the stepped surfaces.

Surface Science
Room 134/135 - Session SS2-MoP
Surfaces and Interfaces Poster Session

SS2-MoP1 Effects of Na and Se Annealing on CuInSe2 Single Crystals*, V. Lyakhovitskaya, K. Gartsman, **Y. Feldman**, H. Cohen, D. Cahen,* Weizmann Institute of Science, Israel

We report on X-ray photoelectron spectroscopic, secondary ion mass spectroscopy, scanning electron microscopy, electron-beam induced current and energy dispersive X-ray fluorescence studies of high quality, travelling heater-grown single crystals of CuInse2, that were subjected to controlled heat treatments from 300 C upwards for varying times, in Se atmosphere, in Na atmosphere and in a mixture thereof. We find that with Na the surface of the crystals is gradually destroyed, while with Se a gradual topotactic type conversion takes place, controlled by Cu diffusion towards the surface, rather than by Se diffusion into the bulk. This is accompanied by formation of a separate Cu-Se phase on the surface. The implications of these findings for the effects of Na on the performance of CuInse2-based solar cells will be considered, in terms of both possible surface and bulk effects.

SS2-MoP2 Two-dimensional and Three-dimensional Growth of Ag Islands on a Ge(001) Surface Studied by Photoemission Spectroscopy*, **M. Yamada**, K. Nakatsuji, T. Iimori, S. Ohno,* ISSP, The University of Tokyo, Japan*; Y. Naitoh,* CREST, Japan Science and Technology Corp.*; T. Okuda, A. Harasawa, T. Kinoshita, F. Komori,* ISSP, The University of Tokyo, Japan

Growth mode of Ag thin films on a Ge(001) surface depends on the substrate temperature: two-dimensional (2D) growth is predominant at low temperatures and three-dimensional (3D) growth becomes dominant at room temperature.@footnote 1@ According to the recipe found by the STM study, we prepared samples composed of 2D (monolayer-thick) or 3D (several-monolayer-thick) Ag islands, and investigated their electronic structure by synchrotron radiation photoemission spectroscopy. A clean Ge(001) surface gives a Ge3d spectrum with a shoulder at the low binding energy side, which is due to surface core-level shift (SCLS) of topmost, 2x1 reconstructed Ge atoms. After Ag deposition at 95K, the shoulder disappeared and the LEED pattern changed to 1x1. These facts indicate that the interaction between Ag and Ge atoms is strong enough to destroy the 2x1 reconstruction in the 2D Ag islands. The Ag4d peak was narrow until Ag thickness of 1.3Å, indicating that the Ag-Ag interaction is weak in the 2D Ag islands. Above 1.3Å a new broad component was observed in the Ag4d spectrum, which suggested the presence of 3D Ag islands. The breadth of the new component indicates the strong Ag-Ag interaction in the 3D Ag islands. When Ag was deposited on a Ge(001) surface at room temperature, the LEED pattern remained to be 2x1 and the shoulder due to the SCLS did not disappear in the Ge3d spectrum. The Ag4d band was broad and bulk-like. These facts indicate that Ag grows three-dimensionally and leaves intact most of the clean Ge(001)-(2x1) surface at room temperature. @FootnoteText@ @footnote 1@ F. Komori et al., Surf. Sci., 438 (1999) 123.

SS2-MoP3 Initial Growth of Ag Islands on Ge(001) Surface at Low Temperature*, **Y. Naitoh**, K. Nakatsuji, F. Komori,* ISSP, University of Tokyo, Japan*; K. Seino, A. Ishii,* Tottori University, Japan

The Ag on Ge(001) surface has been an interesting issue for the last decade since suddenly increase of the surface electronic conductivity at 2K was reported.@footnote 1@ It is suggested the interface between Ag and Ge has peculiar electronic state because neither Ag nor Ge bulk have superconductivity. In the latest STM observation@footnote 2@ showed that mono-atomic-layer (ML) thick Ag islands parallel to the dimer-row of the Ge(001) surface and Ag chains along the dimmer direction are formed at the initial stage of the Ag deposition on a 90 K substrate followed by annealing to room temperature (RT). In the present paper, we show the Ag adsorbed sites on Ge(001) surface by STM without annealing to RT. The STM experiments were performed in an ultra high vacuum (below 1x10@super -8@Pa) system. The surface of a Ge(001) crystal, which was cut from n-type Ge(001), was cleaned by several cycles of Ar@super +@ bombardment and annealing. Ag was deposited onto the clean Ge surface at 90K with the rate of 1 ML/min, and then the substrate was moved to the STM unit as keeping the low temperature. Bright dots, which indicate Ag atoms, were observed between the Ge dimer rows. It was found some dots were arranged to form chains along both the dimer row and the dimer direction having intervals of 2a@sub Ge@ (a@sub Ge@=0.4nm) and islands with 2a@sub Ge@ width elongating along the dimer row. As annealing the substrate to RT bright dots disappeared and the conventional Ag chains and islands were found to be formed. This shows Ag sites on Ge(001) surface without annealing to RT are quasi-stable. These were compared with the stable site of Ag on the surface given by the first-principles calculation. @FootnoteText@ @footnote 1@ M. J. Burns et al., Solid State Comm. 51, 865 (1984) @footnote 2@ F. Komori et al., Surf. Sci. 438, 1234 (1999).

SS2-MoP4 In-Situ X-Ray Reflectometry of the Martensitic Transformation of AuCd Alloys*, **H. Shimazu**, S. Shibata, S. Doi, I. Takahashi,* Kwansei Gakuin University, Japan*; T. Ohba,* Shimane University, Japan

Numerous works have been dedicated to the study of meaning of surfaces for bulk phase transitions. For second order transitions, importance of the dimensionality has been understood thoroughly. Thus, an answer for this issue might have been obtained. Compared to such a situation, we must admit that many phenomena at the surfaces for first order phase transitions have not fully been understood. Especially, peculiarity of nucleation and evolution of domains at the surface triggered by the first order bulk transition remain unveiled, although those in bulk have been investigated. The martensitic transformation is a first order phase transition, responsible for shape-memory effects. In a low temperature phase, bulk domains called "variants" appear. On the other hand, the surface exhibits a morphological change (surface relief). Many people consider that the surface relief is a mere termination of the bulk variants. If they are correct, the evolution of the surface relief may start simultaneously as the variants start to evolve. However, as far as the authors' knowledge, there is no accepted study on the relationship between nucleation of the surface relief and that of the bulk variants. In the present paper, we focus on in-situ observations about the surface relief and the micro-variants in the vicinity of martensitic transformations of AuCd alloys: We observed the surface relief by X-ray reflectivity, whereas Bragg reflection gave information on bulk variants.@footnote 1@ An image plate detector was adopted with an X-ray camera.@footnote 2@ Our study revealed peculiar properties on the evolution of the surface relief. They indicated that the surface plays an intrinsic role at the first stage of the martensitic transformation. An aging effect was also detected in the surface diffraction. @FootnoteText@ @footnote 1@ S. Doi and I. Takahashi; Philosophical Magazine A, 80(2000) 1889-1899. @footnote 2@ S. Shibata, S. Doi and I. Takahashi; to be published in Surface Science (2001).

SS2-MoP6 Metastable Crossed Row Structure and Nano-structural Change on TiO@sub 2@(001) Studied by STM*, **R. Tero**, K. Fukui, Y. Iwasawa,* The University of Tokyo, Japan

Atom-resolved structures on a rutile TiO@sub 2@(001) surface were visualized by scanning tunneling microscopy (STM). We have found that a flat ordered structure, which consists of crossed rows along the [110] and the [11-0] directions, can be prepared by annealing an Ar ion-sputtered TiO@sub 2@(001) surface at 850-1050 K under UHV with heating and cooling rates at 7-10 K s@super -1@. Its LEED pattern was identical to that for a {114}-faceted structure proposed in previous studies. The rows had a bleacher-like structure, which formed stairs at both sides with an average slope identical to the {114} face. An atom-resolved STM image showed that units of three bright spots, which were lined perpendicular to the steps, were arranged by 0.65 nm on each narrow step. The crossed row structure was metastable and its stability depended on the degree of the bulk reduction. Structural transformation occurred at much lower temperatures than that for preparing the crossed row structure. Particles with nm scale appeared on the crossed row structure by reannealing the surface under UHV at 400-490 K. The surface was covered up with the particles of 0.9-6 nm in diameter. Adsorption of formic acid on the crossed row structure before reannealing drastically modified the structural transformation. The particle size was distributed to 2-8 nm in diameter after the formic acid-covered crossed row structure was reannealed at 710 K. The stability of the crossed row structures and the mechanism of the particle growth, which depended on the degree of bulk reduction and reaction of adsorbates, will be discussed.

SS2-MoP7 Theoretical Analysis of Short Range Order of Au/Si(100) 5x3.2 Structure*, **Y. Yagi**, K. Kakitani, H. Kaji, A. Yoshimori,* Okayama University of Science, Japan

It is known that the metal adsorbed semiconductor surfaces show various characteristic structures. One of them is the Au adsorbed on Si(100) surface. According to the recent experimental results by STM and LEED, this system shows the 5x3.2 structure.@footnote 1-4@ Au adsorbates and Si substrate atoms form the 5x3 structure. This structure is made up with the "band" structure along the direction of 3 times and the "band" structures arrange with 5 times period in the perpendicular direction. The STM results indicate that the 5x3.2 structure seems to be formed by protrusions called "wall" in the topmost layer on the 5x3 structure. We describe this system by the lattice gas model for adsorbates (adatoms) in the topmost layer on the 5x3 structure with semi-long ranged repulsive interaction and short ranged attractive interactions, assuming that the protrusion is formed by the adsorbate (adatom), and perform Monte Carlo simulation. We obtain the two adsorbate positional correlation functions and the structure factor of this surface system. The obtained theoretical results are compared with experimental ones, in particular, the correlation function obtained from the STM images. Our results reproduce experimental features semi-quantitatively. The degree of ordering in the 3.2 times period does not seem perfect in the STM images and it may be a structure with short range order. The ratio of interactions with temperature and the most probable interaction ratios are determined by the comparison. @FootnoteText@ @footnote 1@X. F. Lin, K. J. Wan, J. C. Glueckstein and J. Nogami, Phys. Rev. B47, (1993) 3671. @footnote 2@G. Jayaram and L. D. Marks, Surf. Rev and Lett., 2 (1995) 731. @footnote 3@H. Minoda, K. Yagi, F.-J. Meyer zu Heringdorf, A. Meier, D. Kahler, and M. Horn von Hoegen, Phys. Rev. B59, (1999) 2363. @footnote 4@R. Hild, F.-J. Meyer zu Heringdorf, P. Zahl and M. Horn-von Hoegen, Surf. Sci. 454-456 (2000) 851. .

SS2-MoP9 Experimental and Theoretical Investigation of Multi-layer Films with Ultra-thin Intermediate Layers*, **I.G. Levchenko,*** Kharkov Aerospace University, Ukraine

The multi-layer films were applied by the ion deposition method. The three-layered and four-layered films consisting of titanium carbide, titanium nitride, chromium nitride, zirconium nitride, carbonitrides, and aluminum oxide with ultra-thin copper and silver intermediate layers were investigated. The total film thickness was ten to twenty five micrometers. The ultra-thin layers were applied between the main layers, the ultra-thin layer thickness being of ten to hundred atomic layers. The main layers were applied at a voltage of one or two hundred volts and the intermediate layers were applied at five to eight hundred volts. The conditions of intermediate layer application ensured creation of the continuous layers. The aim of ultra-thin layers was to provide relaxation in the main layers, to remove the residual stresses, to ensure the high level of adhesion force between the main layers, and to reduce the porosity due to the penetration of ultra-thin layer metal into the main layers. The measurements of the porosity coefficient were performed by electrolytic method using the hydrogen penetration. The porosity factor was found to decrease twice for copper intermediate layers and thrice for the silver intermediate layers. The micro-stress levels were found to be five times less than those for the film of the equal thickness applied without the intermediate layers. The abrasion test had shown the improved wear resistance due to the absence of microchipping as a result of low micro-stress level and high enough film thickness. The main layer application voltage - intermediate layer application voltage ratio was found to be the significant value in reducing a porosity factor.

SS2-MoP10 About the Interface between a Quasicrystal and its Oxide Overlayer*, **V. Fournèe**, J.W. Anderegg, A.R. Ross, T.A. Lograsso, P.A. Thiel,* Iowa State University

When the surface of an Al-Pd-Mn icosahedral quasicrystal (QC) is exposed to air at room temperature, an almost pure alumina overlayer develops across it. The thickness of this oxide is rather small and is similar to the passivating layer on fcc-Al. This is of course an attractive characteristic which, combined with other surface properties like low friction coefficients or low adhesion, makes QC surfaces relevant for technological applications.@footnote 1@ In particular, the low adhesion property, related to a low surface energy, is believed to be influenced by the gradient, through the surface, of the electronic density of states at the Fermi level (N(EF)). This assume that the low N(EF) characteristic of the bulk electronic structure of QC is effectively maintained up to the surface. However, in a practical situation where an aluminium oxide overlayer is formed, the interface just under the oxide may be depleted in Al and enriched in Pd and Mn. The concentration may be shifted out of the stability range of the QC phase and structural transformation may occur. This also should affect the electronic properties at the interface. In an effort to clarify this point, we will present our recent experimental results on this subject. Experiments were performed on a five-fold surface of a single grain Al-Pd-Mn icosahedral QC. The clean surface was prepared in UHV and later oxidized in-situ. A depth profile of the chemical composition across the oxidized surface is acquired both by Auger and photoelectron spectroscopies. Informations on the morphology of this surface are derived from both scanning electron and scanning tunneling microscopies. Finally, an analysis of the photoelectron core-level lineshape, as a function of the escape depth of the photoelectrons, provides insight into the variations of the metallic character through the surface. @FootnoteText@ @footnote 1@ P.A. Thiel, C. J. Jenks, A. I. Goldman, in Physical properties of Quasicrystals, ed. Z. Stadnik (Springer Verlag, Berlin, 1999).

SS2-MoP11 Temperature Effect of Well-ordered Al@sub2@O@sub3@ Film on NiAl(110)*, **T.T. Lay**, M. Yoshitake, B. Mebarki,* National Institute for Material Science, Japan

It is known that the oxidation of the (110) surface of intermetallic compound NiAl leads to the formation of a well-ordered Al@sub2@O@sub3@ film.@footnote 1@ It has the potential of application in metal-insulator-metal(M-I-M) electron emitter which needs wide gap insulator. In our previous work epitaxial ultra-thin Al@sub2@O@sub3@ film was grown on NiAl(110) by introducing 1200L oxygen at 570K and subsequent annealing at 1070K. The crystalinity of the epitaxial film varied from pressure 5 x 10@super-7@ to 5 x 10@super-8@ Torr. The best crystalinity was obtained when oxygen was introduced at pressure of 5 x 10@super-8@ Torr. However, to get 1200L oxygen at 5 x 10@super-8@ Torr, the time needed is 400minutes. For thick epitaxial Al@sub2@O@sub3@ film, multi-oxidation is required and time needed to growth desire film thickness is too long. To get well-ordered thick expitaxial Al@sub2@O@sub3@ film in higher growth rate, we have carried out the temperature control in oxidation. Oxidation temperature varied from 570K to 720K at constant pressure of 5 x 10@super-7@ Torr for 1200L. After oxidation subsequent annealing is performed at 1070K in a vacuum chamber equipped with LEED/AES. From the LEED pattern, the crystalinity of epitaxial Al@sub2@O@sub3@ film become distinct as temperature increases and shows optimum at temperature around 670K. AES measurement also has good correlation with the results of LEED patterns. The ratio of O/Ni peak intensity is directly related to film thickness.@footnote 2@ The optimum ratio of O/Ni was obtained at temperature around 670K and approximately equal to several multi-oxidations at pressure 5 x 10@super-8@ Torr at 570K. The result shows crystalinity and thickness can be control by oxidation temperature. @FootnoteText@ @footnote 1@ R.M. Jaeger, H.Kuhlenbech, H.J.Freund, M.Wuttig, W. Hoffmann, R. Franchy and H. Ibach, Surf. Sci., 259,235(1991) @footnote 2@ M. Yoshitake and B. Mebarki, 6th. Int.Symposium on Advanced Physical Fields, Tsukuba, Japan, March 6-9, 183(2001)

SS2-MoP12 Initial Growth and Alloy Formation of Ni Ultrathin Films on Pt(111)*, **C.W. Su**,* National Taiwan Normal University, Taiwan, R.O.C.*; Y.E. Wu, C.S. Shern,* National Taiwan Normal University

Low-energy electron diffraction (LEED), Auger electron spectroscopy (AES) and Ultraviolet photoelectron spectroscopy (UPS) were used to study of the initial growth of Ni ultrathin films on Pt(111) at room temperature. As the coverage of Ni between 0.3 ML to 1.0 ML , a (@sr@(3)*@sr@(3))R30°

commensurate structure was observed. As the coverage increases from 1 ML to 1.2 ML, the superposition of Pt(1x1) and epitaxial Ni(1x1) LEED pattern is formed. When the coverage of Ni increases from 1.3 ML to 6 ML, the structure is changed to the incommensurate epitaxy with fine satellites around the (1x1) hexagonal LEED pattern. Deposition of Ni films more than 7 ML up to 12 ML, the p(2x2) LEED pattern is appeared gradually. After high temperature annealing, the formation of Ni-Pt alloy with different coverages of Ni was confirmed by AES and UPS. The starting temperature of alloy formation increases as the coverage of Ni increases. The density of state also shows some interesting changes during the thermal annealing process.

SS2-MoP14 Photoemission from Graphite Overlayers on SiC(0001)*, T. Balasubramanian,* Lund University, Sweden*; T. Kihlgren, L. Walldén,* Chalmers University of Technology, Sweden*; R. Yakimova,* Linköping University, Sweden

For lack of large graphite crystals with well defined termination overlayers of the material prepared by heating SiC can provide an attractive alternative to natural crystals or to samples of highly oriented pyrographite, which is often used as substrate for adsorption and absorption studies. Using LEED, STM and UPS (20 to 140 eV photon energy) for sample characterization we find that heating (2200 K, 1/2 h) an off axes (8 degrees) 4H-SiC(0001) produces a well ordered, multilayer thick overlayer, which shows a 3-fold LEED pattern and gives quite well resolved photoemission spectra. We use the latter to monitor the dispersion of valence electrons, photoemission line widths and cross sections. Particularly narrow emission lines are observed for the Fermi level electrons near K-H in the Brillouin zone and for the upper @sigma@ state at the zone center. Of interest for adsorption studies is that the latter gives a line width on par with that of the C 1s core level.For an on axes 6H-SiC(0001) crystal a similar preparation procedure yields a 6@sr@3x6@sr@3 LEED pattern and photoemission spectra with no dispersion along the c-axes for the @pi@ state, which indicates that the overlayer in this case is a single graphene layer. Such a layer in vacuum should be a zero gap semiconductor with a band crossing at K defining the Fermi level. For the adsorbed monolayer we find that the bands do not cross but form a 0.2 eV gap centered 0.35 eV below the Fermi energy. The gap splits of a thin electron gas with a filled band width of 0.25 eV and an estimated surface density corresponding to 0.06 electrons per C atom.For both mono- and multilayers the photoemission cross sections are oscillatory with nearly out of phase variations for the @pi@ and @sigma@ states when plotted versus the kinetic electron energy and the curves shifted to around 5 eV higher energy for the monolayer.

SS2-MoP15 Local Tunneling Barrier Height Measurement of Cs Monolayer on a Pt(111) Surface*, Y. Yamada,* *A. Sinsarp, M. Sasaki, S. Yamamoto,* University of Tsukuba, Japan

The local tunneling barrier height (LBH) image of the Cs monolayer on a Pt(111) surface is measured in atomic resolution by means of an STM technique. The Cs atoms form three different superstructures, (2x2), (@sr@3x@sr@3) and (@sr@3x@sr@3)R30, depending on its surface coverage on the Pt(111) surface. We find that the (2x2) structure is thermally stable at room temperature in contrast to other structures which disappear in few hours. Only for the (2x2) structure, we could obtain a clear atom-resolved STM/LBH image at room temperature. We find the atomic LBH distribution in the image corresponding to atomic geometry of this structure. This distribution, however, cannot be considered to be identical to the distribution of the classically defined work function. The average barrier height of this structure is, however, about 2.2eV smaller than that of a clean Pt(111) surface, suggesting the work function reduction of about 4.4eV from the clean Pt(111) value. This agrees well with our macroscopical work function results measured by means of the Kelvin contact potential method. The (2x2) surface corrugation amplitude obtained from the STM image is as large as 0.6Å, suggesting that the spatial distribution in the electron density of this structure is strongly localized, in contrast to the case of other 'metallic' superstructures, where no atomic image is observed by STM. It is speculated that the charge localization with some charge transfer causes the lowest work function of the (2x2) structure and its high thermal stability.

SS2-MoP16 Dynamics and Thermal Stability of Cs Super-structures on a Pt(111) Surface*, T. Kondo,* *H. Kozakai, T. Sasaki, S. Yamamoto,* University of Tsukuba, Japan

Understanding the dynamics and the thermal stability of alkali-metal atoms adsorbed on a metal surface is essentially important for controlling the monolayer growth and unveiling the origin of the work function reduction due to adsorption. We have made clear the dynamics from formation to destruction and the thermal stability of the Cs super-structures on a Pt(111) surface by means of Helium atom scattering (HAS) which enables us to study at high sensitivity the dynamics of the ultra-thin delicate layer of Cs atoms. Among three structures previously identified by LEED, both the (@sr@3x@sr@3) and the (@sr@3x@sr@3)R30° structures are found unstable and destructed at around 350K, transforming into the more stable (2x2)structure. The (2x2) structure which is stable up to about 450K exhibits a large corrugation of the potential energy surface seen by He atoms. This suggests a strong bond between Cs and Pt atoms and the localization of electron cloud density for the (2x2) structure as a result of the charge transfer from Cs atoms to the substrate Pt(111) surface. It is also suggested that the work function minimum, attained at the Cs coverage 0.25 forming the (2x2) structure, is closely related to this charge transfer. On the contrary, the small corrugation for the (@sr@3x@sr@3) structure at a full coverage indicates that a bond among adsorbed Cs atoms is metallic, the electrostatic potential being delocalized along the direction parallel to the surface.

SS2-MoP17 ARPES Study of 2x2 Mn-Pt(111) Surface Alloys*, F.J. Palomares,* *P.P. Martin, H. Isern, M. Alonso, F. Soria,* Instituto de Ciencia de Materiales de Madrid (CSIC), Spain

The annealing of metallic layers grown on single crystal substrates has enabled the synthesis of ordered surface alloys and metastable phases non existing in the bulk diagram. This behavior has been reported for the Mn-Pt(111) interface, for which two apparently different 2x2 surface ordered alloys are identified as temperature increases. Angle-resolved photoelectron spectroscopy with synchrotron radiation has been used to study the electronic structure of thin films of these two alloys. Normal and off-normal emission geometries are investigated, for photon energies in the range of 12 to 70 eV. The corresponding results are analyzed in comparison with those from the starting Pt(111)-1x1 surface. Our data confirm that such alloy phases exhibit distinct electronic features, which are discussed taking into account the properties calculated for related systems.

SS2-MoP18 Kinematic Analysis of a Dispersion Region Probed in High-resolution Electron Energy-loss Spectroscopy*, T. Inaoka,* Iwate University, Japan

In high-resolution electron energy-loss spectroscopy (HREELS) with the specular-reflection geometry, a probed dispersion region determined kinematically depends upon the incident angle @alpha@ and the incident energy E@sub 0@. With change in @alpha@ and E@sub 0@, we make a kinematic analysis of the probed dispersion region with special attention to its width. Simultaneously, we evaluate the effect of the image force and the analyzer aperture on the probed region. Our analysis shows that, with a grazing angle @alpha@ fixed and with E@sub 0@ varied in a broad range, we can scan a sharply narrowed probed region on the wavenumber-energy (Q-@omega@) plane to make a close observation of the dispersion relation of surface-excitation modes. Even at grazing incidence, the image force has no substantial influence on the probed region, though it operates to reduce the energy-loss intensity remarkably at low E@sub 0@. When the parameter h@omega@/2E@sub 0@ becomes appreciable compared with the aperture angle, presence of the aperture causes a certain decrease in the width of the probed Q region. In the HREELS with the off-specular geometry, the incident energy E@sub 0@ is restricted to a lower range to insure sufficient intensity, and the probed dispersion region depends upon @alpha@ and an off-specular angle @theta@. With change in @alpha@ and @theta@, we make the same analysis of the probed dispersion region with close attention to its width as in the specular-reflection geometry. The results of this analysis for the off-specular geometry will also be reported at the conference.

SS2-MoP19 Spectroscopic Ellipsometry in the Infrared Range Applied on HF-cleaning*, J.-C. Cigal,* *G.M.W. Kroesen,* Eindhoven University of Technology, The Netherlands

Spectroscopic ellipsometry is a powerful non-destructive diagnostic tool for the study of interfaces and layered systems. By combining this method with Fourier transform infrared spectroscopy one can obtain information on the physical parameters of a complex surface like the complex refractive index, and the thickness of the different layers of the system, and on its chemical composition. We report the design of an ellipsometer running on the principle of rotating compensator ellipsometry. This technique offers many advantages compared to other photometric methods. Among them are the non-ambiguous determination of the ellipsometric parameters and the self-calibration of the apparatus. The imperfect components of the different optical elements are taken into account in the calculation algorithms. To illustrate the performance of such an ellipsometer we will clean a silicon wafer with hydrogen fluoride. The surface will be H-passivated. The wafer will be then exposed to open air. The goal of this experiment is to demonstrate the sensitivity of the instrument by analyzing the first steps of the oxidation of the silicon surface.

SS2-MoP20 Surface Structure Influence on Reactivity of Small Molecules on SrTiO@sub 3@(100) Surfaces*, L. Wang,* Pacific Northwest National Laboratory, usa*; K.F. Ferris,* Pacific Northwest National Laboratory, us*; M.H. Engelhard,* Pacific Northwest National Laboratory

Interactions of water, methanol and HCOOH with stoichiometric, stepped, and reduced SrTiO3(100) surfaces have been studied using temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), and electronic structural calculations. Comparison of TPD spectra and equilibrium adsorption geometries for H2O on SrTiO3(100) with unreconstructed TiO2 (110) and (100) surfaces reveals the structural influence on the water adsorption and desorption behavior. A unique geometric arrangement of surface atoms on stoichiometric (TiO2-terminated) SrTiO3(100) surfaces due to the lack of surface bridging oxygen atoms results in very different adsorption and desorption properties of H2O on SrTiO3(100) compared to TiO2 (110) and (100) surfaces. Electronic structure calculations show that stepped SrTiO3(100) surfaces enhance the localized interaction between the adsorbed molecule and the oxide surface. No reaction products were observed at above 400 K for methanol on annealed stepped SrTiO3(100). However, reactivity of methanol on SrTiO3(100) surfaces are enhanced for the reducing SrTiO3(100) surfaces prepared by Ar+ sputtering. Reaction products of H2, CH4 and CO were observed at above 400 K on the reduced SrTiO3(100) surface. Formic acid was dissociated to form formate and a surface proton below 250 K on SrTiO3(100) surfaces. Formate was decomposed primarily through dehydration to produce CO and H2O, instead of through dehydrogenation to produce CO2 and H2. Different reaction pathways were observed for formaldehyde formation from formic acid on SrTiO3(100) surfaces. On stoichiometric and stepped surfaces, formaldehyde was produced through bimolecular coupling of two formates. However, on reduced surfaces, formaldehyde formation involves the reduction of surface formate by the oxidation of reduced Ti cations.

SS2-MoP21 Anomalous Growth of Ba on Ag(111)*, **O.M.N.D. Teodoro**,* New University of Lisbon, Portugal*; J. Los,* FOM- Institute for Atomic and Molecular Physics, NL*; A.M.C. Moutinho,* New University of Lisbon, Portugal

The deposition of alkalis or earth alkali elements on other metals often produce a well-known decrease of the surface's work function. Such films make possible to achieve work function values lower than 2 eV. These surfaces found applications, for example, in long life cathodes or in negative ion converters. When these electropositive elements are adsorbed the work function drops steeply and reaches a minimum at coverage lower than 1 monolayer. Then, it increases slightly and the work function converges to the value of the deposited element. In this work, we report an anomalous behavior found during the deposition of barium on an Ag(111) surface. After the minimum of about 2.4 eV the work function did not increase up to 2.7 eV, the bulk barium work function, no matter the amount of barium deposited. These results were corroborated by Auger Electron Spectroscopy where we measured a permanent and constant intensity of the Ag MNN peak for high coverages of barium. To explain this anomalous growth of barium on Ag(111) we propose a model based in the diffusion of silver atoms to the barium film. Details of this model will be presented. Further experiments, showed that co-adsorption of oxygen before a second deposition of barium blocked the diffusion allowing the work function to reach the value of 2.7 eV.

Surface Science
Room 134/135 - Session SS3-MoP
Clusters and Aerosols Poster Session

SS3-MoP3 A Study on the High Rate Deposition of MgO Films Synthesized by Pulsed DC Magnetron Sputtering Process*, **Y.M. Chung**,* Sungkyunkwan University, South Korea

Magnesium Oxide (MgO) with a NaCl structure is known to exhibit high secondary electron emission, excellent high temperature chemical stability, high thermal conductance and electrical insulating properties. MgO films are very useful as a buffer layer for the deposition of high Tc superconducting and perovskite-type ferroelectric films, and as a protective layer for AC-plasma display panels to improve discharge characteristics and panel lifetime. For these purposes, the deposition and characteristics of the MgO films have been intensively studied by means of E-beam evaporation, Molecular Beam Epitaxy (MBE) and Metalorganic Chemical Vapor Deposition (MOCVD). However, there have been some limitations such as low deposition rate, micro-cracks during deposition process, and high erosion rate caused by ion bombardment in the glow discharge of AC-PDP. To improve these drawbacks MgO films were deposited on the dielectric substrates by pulsed DC magnetron sputtering with Mg and MgO targets. We have investigated the plasma states with various pulsed DC conditions, partial oxygen pressure and the deposition temperatures by Langmuir probe and Optical Emission Spectroscopy (OES). In order to confirm the relationships between plasma states and film properties deposition rate, microstructure, surface morphology, and composition were analyzed by Î±-step profilometer, XRD, TEM, AFM, and XPS.

SS3-MoP4 The Surface Modification of PZT by Ion Bombardment*, **J.M. Choi**,* Samsung Advanced Institute of Technology, Korea*; H.I. Lee,* Korea Research Institute of Standards and Science (KRISS)*; J.C. Lee,* Samsung Advanced Institute of Technology, Korea, R. of Korea*; D.W. Moon,* Korea Research Institute of Standards and Science (KRISS), Korea

The surface of PZT (Pb@sub 1.0@Zr@sub 0.4@Ti@sub 0.6@O@sub 3.0@) film is modified by ion bombardment or reactive ion etching (RIE) process.@footnote 1,2,3@ In this work, Auger electron spectroscopy (AES),X-ray photoelectron spectroscopy (XPS), medium energy ion scattering spectroscopy (MEIS) and transmission electron microscope (TEM) were adapted to quantitatively analyze the modified surface layer. The AES and XPS depth profiles always show a rapid decrease of Pb intensity in the initial stage of sputter depth profiling, which has been known as the results of surface segregation of Pb@footnote 3@. But MEIS and TEM clearly showed that it is due to the formation of Pb depleted layer due to Pb preferential sputtering. The reduction of Pb concentration in the modified surface layer was about 30% and the thickness of Pb depleted layer was about 13nm by MEIS, in agreement with a 13.2nm thick amorphic layer observed by TEM. XPS spectra showed that Pb 4f shifted to the metallic phase, whereas Zr 3d and Ti 2p shifted to the ZrO@sub 2@ and TiO@sub 2@ phase. Preliminary results on recovery of the Pb depletion by electron beam bombardment and thermal treatment will be reported. @FootnoteText@ @footnote 1@Sharmila M. Mukhopadhyay and Tim C.S. Chen. J. Appl.Phys. 74(2),872(1993).@footnote 2@June Key Lee et al. Appl. Phys. Lett.75,No.3,334(1999).@footnote 3@Yin-yin Lin,Qin Liu,Ting-ao Tang and Xi Yao. Appl. Surf. Sci.165,34(2000).

SS3-MoP5 Formation of Boron-carbon Binary Clusters by Reactive Molecular Ion Irradiation*, **H. Yamamoto**,* Japan Atomic Energy Research Institute, Japan*; T. Saito,* Japan Atomic Energy Research Institute, JAPAN*; H. Asaoka,* Japan Atomic Energy Research Institute

We have observed boron-carbon clusters (B@sub n@C@sub m@) emitted from a boron surface under irradiation of reactive molecular ions, such as C@sub 6@F@sub 5@@super +@, at 2-8 keV, 1µmA/cm@super 2@. In our previous work, enhanced silicon (Si@sub n@@super +@, n@<=@8) and carbon (C@sub n@@super -@, n@<=@12) cluster formation have been observed emitted from an Si(100) and graphite surface under irradiation of molecular SF@sub 5@@super +@ ions at 4 keV, 1µmA/cm@super 2@.@footnote 1@ In both clusters, the intensities of n=4 and 6 are relatively higher than those of the neighboring clusters. Silicon-carbon binary cluster was also observed by the irradiation of C@sub 6@F@sub 5@@super +@ to Si(100) surface. However, Si@sub n@C@sub m@ binary clusters which contain more than two carbon atoms (m@>=@2) were scarcely observed.@footnote 2@ In the present study, B@sub n@C@sub m@ binary clusters are formed through the reaction between the irradiated ion and target atoms. The observed clusters show a yield alternation between odd and even number of constituent atoms. The intensities of n+m=4 and 6 clusters are relatively higher than those of the neighboring clusters even at the present condition. The intensities of the B@sub n@C@sub m@ clusters (m@>=@2) are also higher than those of Si@sub n@C@sub m@ (m@>=@2). It can be considered that the B@sub n@C@sub m@ (m@>=@2) clusters are more stable than Si@sub n@C@sub m@ (m@>=@2) since the diameter of the boron and carbon atoms are not so different.. @FootnoteText@ @footnote 1@ H. Yamamoto and Y. Baba, Surf. Sci., 433-435 (1999) 890. @footnote 2@ H. Yamamoto and H. Asaoka, Appl. Surf. Sci., 169-170 (2001) 305.

SS3-MoP8 Controlled Surface Charging in XPS as a Tool for Fine Structural Analysis*, **H. Cohen**,* The Weizmann Institute of Science, Israel

Surface charging in XPS can seriously smear chemical information. On the other hand, it frequently provides valuable structural and electrical information. Can the controlled surface charging (CSC)@footnote 1@ become a quantitative tool? What are the limits of this probe in terms of spatial resolution, reliability and applicability? These questions and others are discussed in view of supporting experimental results. Enhanced capabilities for structural analysis, down to nm resolution, are demonstrated. @FootnoteText@ @footnote 1@ Nature 406, 382 (2000); JACS 122, 4959 (2000).

Thin Films

Room 134/135 - Session TF-MoP

Multilayers and Thin Film Characterization Poster Session

TF-MoP1 The Interfacial Reaction in the W/WN@sub x@/poly Si@sub 1-x@Ge@sub x@ with Ge Contents and Annealing Process*, **S.-K. Kang**, J.J. Kim, D.-H. Ko,* Yonsei University, Korea*; H.B. Kang,* Sungkyunkwan University, Korea*; T.H. Ahn, I.S. Yeo,* Hynix Semiconductor Inc., Korea*; T.W. Lee, Y.H. Lee,* Ju-Sung Eng., Korea

As CMOS device dimensions are continuously scaled down to achieve high performance, new gate structures with low resistivity materials are required to enhance the electrical properties. In order to reduce the resistivity of gate electrode materials, metal silicide/poly Si structures have been employed. However, with metal silicide/poly Si structures, it is difficult to obtain low gate resistance in a narrow gate line. As a low resistivity gate electrode, metal/barrier/poly Si or poly Si@sub 1-X@Ge@sub X@ gate stack is one of the candidates for the gate structures in the high performance CMOS-FET. In addition, poly Si@sub 1-X@Ge@sub X@ films have been suggested as a promising alternative to the poly-Si gate electrode for CMOS technology due to the low resistivity, variable workfunction, and compatibility with Si processes. In order to investigate the interfacial reactions in the W/WNx/Poly Si1-xGex structure, poly poly Si@sub 1-X@Ge@sub X@ films with 0%, 20%, and 60% Ge content were deposited using LPCVD (EUREKA 2000, Ju-Sung Co. Ltd.) on the 8in silicon wafers. Following the deposition process of poly Si@sub 1-X@Ge@sub X@, WNx and W films were deposited using sputtering method. To study the interfacial reactions in the W/WNx/Poly Si@sub 1-X@Ge@sub X@ with Ge contents in poly Si@sub 1-X@Ge@sub X@ and annealing process, the films were annealed at temperatures between 600°C and 900°C in N@sub 2@ ambient. The interfacial reactions in the W/WNx/poly Si@sub 1-X@Ge@sub X@ films were observed by AES, XPS, HR-TEM, and EDX. After annealing treatment, N composition decreased in WNx and the interfacial layer was formed between WNx and poly Si capping layer. The interfacial layer was expected to be composed of W, Si, Ge, and N by the analysis of XPS and EDX. In addition, the formation of interfacial layer with the increase of Ge contents in poly Si@sub 1-X@Ge@sub X@ will be discussed.

TF-MoP2 The Role of Interfaces in Fe/W and Co/W Multilayers*, **E. Majkova**, A. Anopchenko, Y. Chushkin, M. Jergel, S. Luby, R. Senderak,* Institute of Physics SAS, Slovak Republic

With GMR multilayers (MLs) the attention has been mostly paid to the combinations of transition metals with Ag, Au and Cu. Due to the immiscibility of constituents the multilayer interfaces are chemically sharp, formation of magnetically dead layers at the interfaces is suppressed and electron transport does not suffer from additional scattering phenomena. For applications, the use of refractory metals (W, Mo) as non- magnetic spacer provides an interesting alternative. In this paper the interfaces in e-beam deposited Fe/W and Co/W multilayers (MLs) with 5 and 10 periods and magnetic layers 1 or 2nm thick are studied. For analyses the X-ray diffraction (XRD), X-ray reflectivity (XRR) and diffuse scattering at grazing incidence (GIXDS) completed by simulations of the spectra were used. All MLs showed regular periodic structure with layer thicknesses close to the nominal values. The interfacial roughness was 0.5-0.7nm, slightly higher for W/on- Co or W/on -Fe interfaces. >From the GIDS spectra vertical correlation of the interfaces across the whole ML stack was obtained. The XRD patterns revealed polycrystalline structure of the Fe, Co and W layers with structural coherency between fcc Co(111) and/or bcc Fe(110) and bcc W(110) lattice planes across the ML stack. The coherency is affected by the lateral waviness of the Fe/W or Co/W interfaces what results in relatively wide angular distribution of the column orientation. The data point at the growth induced mixing and roughness at the ML interfaces. There is no evidence of compound formation at the interfaces even at the deposition at elevated temperatures (<=200C). The miscibility of Co/W and Fe/W systems and the possible formation of magnetically dead layers due to the mixing and/or roughness at Fe/W and Co/W interfaces are discussed.

TF-MoP3 Intermixing Phenomena in Immiscible Ag/Co Bilayers and Co/Ag/Co Trilayers under KrF Laser Annealing*, **S. Luby**, E. Majkova, M. Jergel, R. Senderak,* Institute of Physics SAS, Slovak Republic*; P. Mengucci, G. Majni,* Uni. Ancona, Italy*; E. D'Anna, G. Leggieri, A. Luches, M. Martino,* Uni. Lecce, Italy

The discovery of GMR in multilayers of immiscible pairs of metals or alloys is the stimulus for the progress in the field of microdevices. Consequently, the study of the thermal stability of GMR structures becomes topical. In the last years a couple of papers on excimer laser induced diffusion in layered structures appeared. In one of them we have studied intermixing in Co/Ag/Co trilayers under XeCl laser thermal treatment. In this paper we have employed thermally more effective KrF laser and the processed structures were composed of layers only several nm thick. Bilayers and trilayers were e-beam deposited in UHV at room temperature onto oxidized Si substrates. The samples were processed by fluences F=0.1-0.25 Jcm@super -2@ with number of pulses @<=@1000 directed to the same irradiation spot.The samples were studied by RBS, XRD, grazing incidence XRD, X-ray reflectivity and sheet resistance measurements. The temperature and depth of melting vs. time in irradiated structures was obtained by numerical computations. Using a broad interval of heat treatments we were able to study the intermixing phenomena at various interfaces. At solid- solid interfaces the grain boundary diffusion of Ag into Co layers dominates the intermixing. The preexponential factor and activation energy of diffusion are D@sub 0@ ~ 10@super -10@ m@super2@s@super-1@ and E= 0.4 eV. At solid liquid interfaces the sharpening of previously deteriorated profiles (probably by back diffusion in immiscible systems) was observed at F=0.2 Jcm@super -2@. Here, the value E=1.5 eV was typical. The jumping of Ag clusters seems to be an explanation of the observed value. Using liquid-liquid interactions granular Ag-Co films were obtained. The phenomena in laser treatment are complex, however, they provide more degrees of freedom due to the controlled depth of melting and delivery of energy in well-defined quanta.

TF-MoP4 The Study of Growth of Al on Polyimide Free-standing Films*, **X.-F. Lin**,* Charles Evans & Associates*; D.A. Grove,* Luxel Corporation*; T.F. Fister, L.P. Bisaha, G.S. Strossman, L.-C. Wei,* Charles Evans & Associates*; G. Lefever-Button,* Luxel Corporation*; J.R. Kingsley, I.D. Ward, R.W. Odom, P.M. Lindley,* Charles Evans & Associates

Al thin film growth on polyimide free-standing films has been studied by several different characterization techniques. We focused our attention on investigating Al growth, nucleation, and the resulting surface structures. Atomic force microscopy (AFM) and energy dispersive x-ray spectroscopy (EDS) were used to monitor surface morphological evolution and variations of stoichiometries of the Al/polyimide complex as a function of the increasing thickness of Al thin films. The chemical bonding states between Al and polyimide complex were obtained by using x-ray photoelectron spectroscopy (XPS); while the local surface electronic density distribution about the Fermi-level was revealed by scanning tunneling spectroscopy (STS) measurements. We found that during the initial interaction between the condensing Al adatoms and the polyimide substrate, the Al adatoms interact with carbonyl groups of the polyimide to form small clusters which conform to the surface morphology of the polyimide film. Further Al growth produces oriented crystallized sub-micron islands that enlarge with additional Al deposition. The STS I-V spectra acquired at different stages of Al growth show variations of local surface electric conductivity which are affected by adsorbate-substrate and adsorbate-adsorbate interactions, as well as external environmental conditions. These results are compared for Al grown on both free-standing and Si substrate-supported polyimide films.

TF-MoP5 Amorphous Silicon Photodiodes for Image Sensing*, M. Ristova,* Texas A&M University and University in Skopje, Republic of Macedonia*; **Y. Kuo**, H.H. Lee, S. Lee, J.Y. Tewg,* Texas A&M University

The aim of this research was to develop amorphous silicon (a-Si:H) thin film photodiodes for image sensing using the He-Ne (632 nm) laser source. Three different kinds of thin film diode structures, i.e., metal-(a-S:H)-metal, n@super +@-(a-S:H)-metal, and n@super +@-(a-S:H)-n@super+@, were prepared. The a-Si:H (between 200 and 1000 nm) and n@super +@ (20 nm) layers were deposited by plasma-enhanced chemical vapor deposition (PECVD) at 250°C. The molybdenum metal was deposited with a magnetron-sputtering gun at 13.56 MHz. All a-Si:H layers, which contain about 10 % of hydrogen, were deposited under the same condition. The n@super +@ layer's conductivity was about 2.3E10 (ohm-cm)@super -1@, while the conductivity of the undoped a-Si:H was about 1-2E9 (ohm-cm)n@super -1@. The complete diode was fabricated using photolithography and reactive ion etching (RIE) methods. Factors, such as electrode geometry, contact resistance, a-Si:H thickness, and the thermal treatment, were studied for their influence on the diode performance. The diode's dark and illumination currents, i.e., I@sub dark@ and I@sub illumination@, were determined from current-voltage (IV) measurement. The following conclusions are summarized from this study: 1) the highest current (in either dark or under illumination condition) can be obtained with the pattern with highest value for the ratio between the illuminated area and the average distance between the gridlines 2) the contact resistance can be the dominating factor in the current path, 3) the thick film has the large light absorption efficiency and the high current ratio, and 4) the annealing step repairs the RIE damaged film and greatly improves the diode performance.

TF-MoP6 Li3PO4:N/LiCoO2 Coatings for Thin Film Batteries*, M.E. Gross,* *P.M. Martin, D.C. Stewart, J.W. Johnston, C.F. Windisch, G.L. Graff,* Pacific Northwest National Laboratory*; P.L. Rissmiller, E.L. Dudeck,* Mine Safety Appliances Company

Li@sub 3@PO@sub 4@:N/Li@sub 1.04@CoO@sub 2@ thin film battery structures were deposited by reactive RF magnetron sputtering. Li@sub 3@PO@sub 4@:N (LIPON) thin films up to 1 µm thick were deposited using a 6" diameter Li@sub 2.9@PO@sub 3.5@ pressed powder target. Li@sub 1.04@CoO@sub 2@ thin films were deposited using a 6" diameter LiCoO@sub 2@ pressed powder target. LIPON films were deposited in He + N@sub2@ mixtures and LiCoO@sub 2@ films were deposited in Ar + O@sub 2@ mixtures. Total chamber pressure during deposition ranged between 10 and 20 mTorr and RF power to the sputtering targets ranged from 100 W to 400 W. Because XPS gave ambiguous compositional results, the films were optimized for AC and DC conductivity. Electrical conductivity was extremely sensitive to deposition conditions (deposition rate, sputtering gas pressure, and reactive gas partial pressure). AC conductivity measurements were made at a frequency of 10 kHz, and were correlated to DC conductivity measurements. LIPON films had highest conductivities in the 130 S.cm@super -1@ range and the highest AC conductivity of Li@sub 1.04@CoO@sub 2@ films was near 0.24 S.cm@super -1@. The most conductive films were deposited at 20 mTorr pressures and 100 W target power. X-ray diffraction analysis showed that the films were mostly amorphous. Films deposited under these conditions were transparent at visible wavelengths with a refractive index of 1.6. Lower conductivity films were brownish in appearance and less transmissive than films with high conductivity. The rechargeable battery structures consisting of a gold cathode, 0.4 Âµm LIPON, 0.6 Âµm Li@sub 1.04@CoO@sub2@, Li metal anode, and Cu substrate are currently under test. The thin film batteries have been cycled successfully. Performance results are correlated with film properties and reported. Future work will involve optimization of battery performance on a large scale and scale up of the deposition process.

TF-MoP8 Degradation Mechanisms of Low-Temperature Poly-Si Thin-Film Transistors with PECVD TEOS Oxide*, H.W. Zan,* *P.S. Shih, T.C. Wu,* National Chiao Tung University, Taiwan*; T.C. Chang,* National Sun Yat-Sen University, Taiwan, Taiwan, R.O.C.*; C.Y. Chang, D.Z. Peng,* National Chiao Tung University, Taiwan

For being applied on low temperature poly-Si AMLCD, we fabricate poly-Si TFTs with PECVD TEOS oxide as gate insulator. It is found that the output characteristics of our devices are well enough with mobility as 37 cm2/V.s and quite low leakage current. However, due to the high density of trap states localized within the grain boundaries, the electric fields across the grain boundaries near the drain side are considerably high even under moderate biases. The hot-carrier effects are therefore more pronounced in poly-Si TFTs than in MOSFETs. To investigate the reliability issues of poly-Si TFTs, we carefully apply several kinds of electrical stresses on our devices and study their degradation phenomena. Two different degradation mechanisms can be concluded. For the stress under linear region, stress-induced defects are located in the whole gate insulator and are uniformly distributed from source to drain. These defects are positive fixed oxide charges and the acceptor-type interface states in the upper half of the band gap. It is also noted that the degradation degree depends on the magnitude of gate current and the electric field across the gate oxide. For stress under saturation region, however, additional defects near the drain side are generated. This asymmetric degradation phenomenon is attributed to the presence of avalanche-generated carriers. These defects could be acceptor-type interface states in the upper half of the bandgap and donor-type interface states in the lower half of the bandgap. In addition, stress under saturation region produces severer degradation than that under linear region.

TF-MoP9 Atomic Force Microscopy Observation of TiO@sub2@ Films Deposited by dc Reactive Sputtering*, T. Takahashi,* ***H. Nakabayashi****, N. Sasai, K. Masugata,* Toyama University, Japan

A bombardment of energetic particles such as secondary electrons and recoiled ions ejected from the target plane is very useful technique for modifying the structure of the film in reactive sputtering. It leads to the interesting effects such as enhancement of reactivity, adatom mobility and atomic peening. Therefore, the state on the surface of the as-deposited film may significantly depend on the bombardment condition. So, in this study, the relationship between the surface morphology and the crystal structure of TiO@sub2@ films has been investigated in detail. TiO@sub2@ films with thickness of about 2-3 µm were deposited by dc reactive sputtering on glass-slide substrates. The crystal structure and surface roughness of films were measured with a X-ray diffractometry and an atomic force microscopy (AFM), respectively. The A(101), A(200), A(112) and A(220) peaks were observed from the X-ray diffraction patterns, where A shows an anatase of TiO@sub2@. With increasing energy and number of bombarding particles, X-ray peak intensities I@subP@ of A(101) and A(200) gradually decreased, and I@subP@ of A(112) and A(220) gradually increased, respectively. A(220) peak was significantly higher than others. The crystallinity of TiO@sub2@ film was highly improved and its crystallite size became larger with an increase of them. The roughness parameter Ra on the surface of TiO@sub2@ films also depended on them. Ra increased in the range of 4 to 51 nm with increasing energy and number of bombarding particles. Consequently, it was found that the surface morphology and the crystal orientation of TiO@sub2@ films strongly affected to the bombardment of energetic particles to the growing film.

TF-MoP10 Effects of Annealing Conditions on Doping Efficiency in the Indium Tin Oxide Thin Films Deposited at Low Temperature*, J.W. Bae,* Sungkyunkwan University, Korea, South Korea*; S.D. Park, D.H. Lee,* Sungkyunkwan University, Korea*; Y.J. Lee,* Sungkyunkwan University, Korea, South Korea*; G.Y. Yeom,* Sungkyunkwan University, Korea

Tin-doped indium oxide (ITO) thin films were deposited on glass substrates at low temperature(below 90°C) by a dual oxygen beam assisted evaporator system and the effect of various annealing conditions such as annealing atmosphere and annealing temperature on tin-doping efficiency affecting electrical, physical, and optical properties of the ITO were investigated. The tin composition of the source was varied by mixing indium oxide and tin oxide(0 wt.% ~ 30wt.%). Two rf oxygen sources mounted in the chamber were used for oxygen ion and radical sources, respectively. Atomic percentages of tin in the deposited ITO thin films were investigated by X-ray photoelectron spectroscopy. Carrier density and Hall mobility changed with the doped tin concentration and annealing conditions were measured by Hall effect measurement. Crystallinity, sheet resistance, and optical transmittance were observed by a X-ray diffractometer, a four point probe, and an UV-spectrometer, respectively. Carrier concentration of the undoped indium oxide (0% tin) thin film deposited at the optimum deposition condition of O/In compositions (by controlling the flux ratios of two rf oxygen sources and the evaporation source) was decreased with annealing but Hall mobility was increased from ~20 cm@super 2@/Vs to 105 cm@super 2@/Vs. On the other hand, in the case of tin doped indium oxide (> 0% tin) film deposited at optimum deposition conditions, both the carrier concentration and the mobility were increased with the increase of the annealing temperature and, therefore, the resistivity was decreased from 5 X 10@super -4@ ohm-cm to below 2 X 10@super -4@ ohm-cm due to the increase of tin doping efficiency. Tin atoms located at interstitial sites during the deposition at low temperature appear to move to indium substitutional sites by annealing. It implies that tin atoms in the indium tin oxide deposited at low temperature could act as impurity instead of dopant.

TF-MoP12 Electrical Properties for Si Doped Glass Light Emitter*, T. Ichinohe,* Tokyo National College of Technology, Japan*; S. Nozaki, H. Morisaki,* The University of Electro-Communications, Japan*; S. Masaki,* Tokyo National College of Technology, Japan*; K. Kawasaki,* TDY Co. Ltd., Japan

Nanometer-sized Si ultrafine particle films (the Si nano-structured films) have been studied extensively as a candidate of Si-based photo-electronic coupled devices. Some of the authors have discussed the emission mechanism of the visible light emission and others have emphasized the possibility on the application to light emitters, although the emission intensity of the Si nano-structured films still remains to be quite low at present. The correlation between the light emission and the carrier injection mechanism in the Si nano-structured films should be clarified to realize Si based light emitter. We have studied both photoluminescence (PL) and electroluminescence (EL) of the Si doped glass (Si-DG) films fabricated by the ion beam sputter-deposition. The transmission electron microscopic(TEM) study has shown that the presence of nano-crystalline Si particles formed by annealing at 900 °C in nitrogen-gas atmosphere is essential for the visible light emission. PL spectra have been influenced by the excitation light energy, indicating that the emission is via the emission centers distributed in the interface between the crystallites and the surrounding SiO@sub 2@. EL devices with indium-tin-oxide (ITO) top electrodes have shown the emission peak at 650 nm, which is considerably longer than the PL peaks between 520 and 580 nm. The EL devices have shown the luminescence only when the diode is in forward bias, that is, the Si back contact is positive to the ITO top electrode. The integrated intensity increases almost in proportion to the injection current. When the forward bias voltage exceeded 5 V, EL became to be strong enough to be noticed with the naked eye in dark. We noticed that EL spectra tend to become broad with increasing current. C-V measurement has shown that the reverse bias characteristics are explained by the MOS-like structure with the flat band potential of about -4V.

TF-MoP14 Characterization of Pb(Zr@sub0.52@Ti@sub0.48@)O@sub3@ Films in the Thickness Range of 0.4-6.0µm Prepared by Pulsed Laser Deposition*, M.C. Kim,* Yonsei University, Korea*; J.W. Choi, S.J. Yoon, H.J. Kim,* Korea Institute of Science and Technology*; K.Y. Yoon,* Yonsei University, Korea

The films of nominal composition of Pb(Zr@sub0.52@Ti@sub0.48@)O@sub3@ (PZT) in the thickness range of 0.4-6.0µm were fabricated on Pt/Ti/SiO@sub2@/Si substrate using a pulsed laser deposition (PLD). The PZT films were deposited at 500°C with single process and post annealed at 650°C in oxygen atmosphere because the deposition rate of PLD was fast. The variations in crystallite orientation, microstructure, and ferroelectric and dielectric properties were determined as a function of film thickness. The preferred orientation (111) was changed to (110) above the thickness of 8000Å. As film thickness increased, gain size increased and cross-sectional microstructure showed columnar structure. Remnant polarizations increased from 20 to 40µC/cm@super2@ approximately, and relative permittivity and coercive field decreased from 1800 to 1000 and 45 to 30KV/cm, respectively. The changes of property would be discussed in terms of the presumed influence of interfacial phenomena.

TF-MoP16 The Effect of the Process Parameters on the Electrical Properties of Ni-Cr-Al-Mn-Si Alloy Thin Films*, B.J. Lee,* Inha University, Korea*; C.S. Kim,* Korea Electronics Technology Institute*; G.B. Park,* Yuhan College, Korea*; D.C. Lee,* Inha University, Korea

We have fabricated thin resistor films using the DC/RF magnetron sputtering of 75wt%Ni-20wt%Cr-3wt%Al-4wt%Mn-1wt%Si alloy target and studied the effect of the process parameters on the electrical properties for low TCR(Temperature Coefficient of Resistance) films. In sputtering process, pressure and substrate temperature, are varied as controllable parameters. The films are annealed to 400°C in air and nitrogen atmosphere. We have investigated the microstructure using TEM, XRD, EPMA and EDS and measured the electrical properties, the sheet resistance and TCR. The oxygen content and TCR of the films decreased as the sputtering pressure decreased. The oxygen content were 8.9, 8.5 and 1.5wt%, TCR were 105, 85 and 54ppm/°C for 25, 15 and 5mTorr of the pressure, respectively. The sheet resistance, TCR and crystallinity of the films increases with increasing the substrate and annealing temperature. The sheet resistance and TCR abruptly increased as annealing temperature increased over 300°C in air atmosphere. >From TEM and XRD, it is found that these results are due to the existence of NiO on film surface formed by annealing. As a results of them, it is suggested that the sheet resistance and TCR of thin films can be controlled by variation of sputter process parameter and annealing of thin film below 300°C in nitrogen.

TF-MoP17 Electrical Properties of the Novel Semiconductor Alloy Cu@sub x@Cd@sub 1-x@Te Prepared by rf Sputtering, *E. Garnett-Ruiz, G. Torres-Delgado, O. Jiménez-Sandoval, R. Perez-Castanedo, P. Garcia-Jimenez,* Cinvestav-IPN, Mexico*; B.S. Chao,* Energy Conversion Devices*;* ***S. Jiménez-Sandoval,*** Cinvestav-IPN, Mexico

It has been demonstrated that the incorporation of Cu into Cd sites at concentrations around 0.3 at% produces high quality films when compared to pure CdTe or to Cu@sub x@Cd@sub 1-x@Te with higher copper concentrations. The improvement on the structural properties produces an important effect on the transport properties of this semiconducting alloy. For instance, we have observed that the resistivity drops 4 to 8 orders of magnitude depending upon copper content. In this work we present the results of a study on the electrical properties of thin films, grown by rf sputtering, of the novel semiconductor alloy Cu@sub x@Cd@sub 1-x@Te as a function of copper concentration. This study is based on the current-voltage characteristics of a capacitor-like structure metal/semiconductor alloy/metal (suitable for measurement of polycrysdtalline materials) which allows to determine the values for electrical parameters when this structure is measured for different thicknesses of the semiconducting material.

TF-MoP18 Characterization of Hydrogenated Amorphous Germanium, a-Ge:H, Thin Films Deposited by a Low Pressure Hollow Cathode Plasma-jet Reactive Sputtering System*, G. Pribil,* *R.J. Soukup, N.J. Ianno,* University of Nebraska, Lincoln*; Z. Hubicka,* Academy of Sciences

Hydrogenated amorphous germanium, a-Ge:H, thin films were deposited by means of a low pressure dc hollow cathode plasma-jet system. A high density plasma was excited in a cylindrical nozzle of polycrystalline Ge working as a hollow cathode. An adjustable magnetic field was used for dc hollow cathode discharge stability and for partial confinement of the reactive plasma at the cathode outlet. The germanium nozzles were reactively sputtered in this high density hollow cathode discharge. Only nontoxic gases, argon and hydrogen, were used as a working gas mixture. Different conditions for the dc hollow cathode system were used for deposition. The a-Ge:H thin films were characterized by FTIR spectroscopy, Tauc band gap measurements, measurements of conductivity in the light and in the dark, and thickness measurements. The growth rate achieved was in the range of from 2 to 6 µm/h. This system has already been used for the deposition of high quality hydrogenated amorphous silicon, a-SiH, thin films using silicon nozzles. These experiments lead to the deposition of hydrogenated amorphous silicon/germanium alloy films, a-SiGe:H, without the use of silane or germane, using co-sputtering of Si and Ge nozzles in a multi-hollow cathode plasma jet system.

TF-MoP19 Metal-insulator Transition in Ultrathin Copper Film Observed By Impedance Spectroscopy*, X. Jin,* *Y. Zhou, Y.H. Hyun, T.-U. Nahm, C.O. Kim, Y.P. Lee,* Hanyang University, Korea

Ultrathin Cu films with a thickness of 0.3- 9 nm were thermally evaporated on a glass at room temperature in an ultrahigh vacuum chamber. The simultaneous in-situ monitoring of the complex impedance spectrum and the electrical resistance of the growing films was carried out. A metal-insulator transition was observed at a percolation onset thickness of 2.5 nm. The complex impedance of the films could be described by a parallel R-C equivalent circuit when the film thickness is smaller than the percolation onset thickness. With the further growth of film, the complex impedance undergoes a transition to an inductive equivalent circuit. A change in the electrical resistance at the percolation onset thickness follows a scaling law R ~ (d-d@sub c@)@super -t@ where t is an exponent, and are consistent with the observed transition.

TF-MoP20 In-situ Buried Multiquantum Well Structures Studied by Photoreflectance and Photoluminescence Spectroscopy*, A. Perez-Centeno,* *M. Lopez-Lopez, M. Melendez-Lira, M. Tamura,* CINVESTAV-IPN, Mexico*; T. Ishikawa,* OTL, Tsukuba, Japan

In this work we present the optical and structural characteristics of AlGaAs/GaAs multiquantum wells (MQWs) that were in-situ etched into mesa-stripe structures and then buried avoiding air-exposure of the active region at the sidewalls. The samples were fabricated using the following steps: First, by conventional photolithography and etching techniques mesa stripe-arrays of different widths and along different crystallographic directions were patterned on the surface of a 250nm thick GaAs protective layer of MQWs grown on a GaAs(001) wafer. The mesas depth was 200nm, in order to protect the MQWs a 50nm-thick GaAs layer was left unetched. Next the wafer was introduced into an UHV multichamber system with an MBE chamber and an etching chamber connected through UHV tunnels. The initial pattern was transferred down to the MQWs by in-situ Cl@sub 2@-etching to a depth of ~200nm. Then, the sample was transferred in UHV to the MBE chamber, where an AlGaAs layer was overgrown thus completing the in-situ buried structures. Photoluminescence (PL) studies showed a decrease in the MQWs PL intensity and PL lifetime for mesa stripes of several microns in width, thus showing the effects of carrier trapping and non-radiative recombination at the etched-regrown interfaces on the sidewalls. The PL degradation was stronger for mesas along the [110] direction. In the photoreflectance (PR) spectra the transitions associated to the MQWs were clearly observed for mesas along [1-1 0], however for mesas along [110] we only observed the signal associated to the GaAs band-gap. PR spectra also showed the presence of oscillations above the GaAs band-gap value associated to built-in internal electric fields. The strength of the internal electric fields was in the order of 10 kV/cm, as obtained by the Franz-Keldysh model. We discuss the degraded optical properties for mesas along [110] in terms of the increased difficulties to smoothly overgrow mesa-sidewalls along this direction.

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Developments in Vacuum Technology Poster Session

VST-MoP1 Optimization for the Design Parameters of Screw-typed Turbo Vacuum Pumps*, R.-Y. Jou,* Tung-Nan Institute of Technology, Taiwan, ROC

A rotor configuration design for the new turbo booster pump which is combined a TMP section with a spiral-groove rotor by a specially designed connecting blade and is proposed by Jou et al.@footnote 1@ and this new design is successfully predicted by both of CFD and DSMC methodologies simultaneously. The computed and tested results show that this pump is effective to operate in an inlet pressure range from 10-7Torr to around 10Torr with a maximum pumping speed approximately 1000L/s in free molecular regime. To investigate the inner pressures and to compare the computed data with experimental one, a measurement system also has been constructed.@footnote 2@ Since the aforementioned rotor geometry is composed of three different sections, a TMP section, a connecting section, and a spiral groove section, respectively, it is very difficult or even impossible to efficiently design the rotor geometry and to optimize its performance. In this paper, rotor geometries with characteristics of varied helical angle and groove depth are modeled using two design curves. These curves can be expressed by two appropriate functions, like polynomials, to meet the different pumping requirements in each different regime. The channel of the rotor is then modeled by the rule surface generated from the two characteristic design curves. Through this geometrical representation, pumping speed and compression ratio for this pump also can then be evaluated by the same computational scheme and same design procedure as previous paper. Analyses are conducted to parameters of the curves to show the optimization of the design. @FootnoteText@@footnote 1@R. Y. Jou et al., Designs, Analyses, and Tests of A Spiral-Grooved Turbo Booster Pump, J. Vac. Sci. Technol., A, 18(3), 1016 (2000). @footnote 2@H. P. Cheng, R. Y. Jou, et al., Inner Pressure Measurement of Turbo Molecular Pump, J. Vac. Sci. Technol., A18(4), 1766 (2000).

VST-MoP2 Two Stage Water Ring Vacuum Pump with Air Ejector Theoretical Analysis and Design Calculation of Gas Flow*, C.W.M. Chen,* Zibo Water Ring Vacuum Pump Factory Co., Ltd., P.R. China, P.R.China

In this essay, the gas flow state and emergence of excitated liquid inside the ejecting tube of the two stage water ring vacuum pump with air ejector are analysed and calculated by the theories and formulas of unary isentropic flow and the characteristical dimension design calculation formulas for the ejector pump are given in accordance with the test and design experiences. It's well known that the air ejector has the features such as simple structure, reliable work, light weight, no mechanical moving parts, i.e., no friction, etc. therefore, it's widely used together with the water ring vacuum pump to form a vacuum air extraction pack to increase the air pumping capacity. For example, when only use the two stage water ring vacuum pump, the work situation point often used is 100-60mbar of suction pressure ,whose lowest pressure is 30~25 mbar (compensation water temperature is 15~20). when used together with the air ejector, the lowest suction pressure is 4~5 mbar. When the suction pressure is 13~15mbar, the air pumping speed is still able to reach 55~60% of the maximum pumping speed of the two stage water ring vacuum pump.this is quite favourable to the work situation which pumps corrosive gas and gas with trace impurity or much steam and requires a larger pumping speed when the suction pressure is 13~15 mbar. Hence, this kind of machine pack is widely used in chemical industry, pharmaceuticals, petrochemical, metallurgy, light industry and so on. Many factories and companies in the world all produce the machine pack formed by two stage water ring vacuum pump with air ejector. The maximum specification has already reached 60~70m@super 3@/min. for example, the pumping speed of glrd 3200 type two stage water ring vacuum pump with air ejector produced by general company in U.K. is 60 m@super 3@/min (suction pressure is 15 mbar). This essay will theoretically analyse and calcucate the gas flow in the ejector pump of such kind of vacuum air pumping machine pack and introduce the calculation ascertainment of its characteristical dimension.

VST-MoP4 Cryogetter Pumping of the Channel of Neutral Beam Injector*, A.N. Dranichnikov,* *A.A. Ivanov, V.S. Khrestolubov,* Budker Institute of Nuclear Research, Russia

In 2000 at the Budker Institute of Nuclear Physics the injector of neutral hydrogen atoms for the RFX device (Padova) was created with equivalent ion beam current up to 2 A, 50 keV energy and 50 ms pulse duration. The pumping of vacuum chamber is provided by two cryogenic priming pumps with pumping speed of 20 m@super 3@/s for each of them. At full gas load about 0.53 m@super 3@/(Pa*sec) the vacuum at beam channel outlet is provided by the cryogenic pumps at a level of 4*10@super -4@ Pa. Cryosorption by using nitrogen allows to keep up the vacuum between successive injection pulses at 1.5*10@super -6@ Pa. Consequently the helium fluid consumption reduces. Filling liquid helium is carried out completely remotely. The design of the cryogenic pumps and the results of the pumping speed measurements are discussed in this report.

VST-MoP5 Peltier Vacuum Gauge@footnote 1@*, D.H. Jung*, *Y.H. Jeong, C.D. Park, S.M. Chung,* POSTECH, S. Korea

The junction of a thermocouple, conventionally used as a temperature sensor, can work as a point heat source or sink if an electric current flows. This characteristic is well known as the Peltier effect. Utilizing the Peltier effect of a thermocouple, we have developed a new type of the vacuum gauge, Peltier vacuum gauge (PVG). PVG is based on thermal conduction by gases, and consists of a single thermocouple that plays roles of the heater and sensor simultaneously. PVG shows the sensitivity similar to, or better than that of the Pirani gauge or convectron gauge in the range between 10@super -4@ torr and atmosphere. However, what distinguishes PVG from these gauges are: (1) it has appreciable sensitivity even above 10 torr due to the fact that it is a point heat source, which allows more effective gaseous conduction spherically in viscous regime, (2) its simple structure offers a way to the miniaturization of a vacuum sensor appropriate for local, and fast probe as the pressure changes, and (3) it operates at a few degrees above the wall temperature with high sensitivity. @FootnoteText@ @footnote 1@ patent applied.

VST-MoP6 Total and Partial Pressure Measuring Devices Not to Be Influenced By Charged Particles from External Environments*, H. Saeki,* *T. Aoki,* Japan Synchrotron Radiation Research Institute, Japan*; K. Tatenuma,* Kaken Co. Ltd., Japan*; T. Momose,* Miyagi National College of Technology, Japan

Some B-A gauges in the SPring-8 storage ring have indicated minus pressures or lower pressures due to influx of photoelectrons produced by synchrotron radiation.@footnote 1,2@ Partial pressures using quadrupole mass spectrometers in the ring have not been measured at stored electron beam current of more than 40 mA. It was found that electrons of more than 1 x 10@super -9@ A at the stored beam current of 70 mA flowed into the head of a quadrupole mass spectrometer. It was also found that B-A gauges using in the ring indicated minus pressures due to influx of electrons of more than 2 x 10@super -10@ A. An automatically removal device of charged particles into pressure measuring devices was designed, composed of electrostatic electrodes and an instrument of charged particles. A self-compensating circuit for a mineral insulated gauge cable@footnote 3@ used in a radiation environment was also designed. Using the automatically removal device and the self-compensating circuit, the practical vacuum gauge system with a self-compensator @footnote 2@ and the quadrupole mass spectrometer will be tested in such a hot vacuum environment and in a radiation environment around accelerators. @FootnoteText@ @footnote 1@H. Saeki and T. Momose, J. Vac. Sci. Technol. A, 18, 244 (2000). @footnote 2@H. Saeki, T. Aoki, H. Yonehara, and T. Momose, J. Vac. Sci. Technol. A, 19, 349 (2001). @footnote 3@H. Saeki, T. Aoki, and T. Momose, to be published in J. Vac. Sci. Technol. A, May/Jun (2001).

VST-MoP7 Development of Axial-Emission Ionization Gauge for XHV Measurement*, Q.D. Sun,* Shanghai Jiao Tong University, P.R. China*; J.Z. Chen,* Shanghai Lamp Factory, P.R. China

An ionization gauge structure, designed as the "Axial-Emission Gauge (AEG)", with the filament and collector plate located on the opposition ends of a helical grid, has many advantages compared to the BA gauge. This unique arrangement gives higher sensitivity (0.28/Pa) lower limiting pressure (2.7x10@super -9@), less divergence in sensitivity between gauges (5%), and it is easier to degas than BA gauge. In order to further lower the limiting measureable pressure of AEG. Five axial-emission type ionization gauges have been developed: the axial-emission self-modulated ionization gauge, the axial-emission suppressor gauge, the axial-emission bent beam, the axial-emission magnetron ionization gauge and the axial-emission magnetron suppressor gauge. In comparison with the conventional gauges, these five AE type gauges have some advantages also same as AEG. All these points make it more suitable for measurement of UHV and XHV.

VST-MoP8 In situ Pressure Measurement in Small Gettered Volumes*, V. Nemanic,* ***M. Zumer****, B. Zajec,* ITPO, Institute of Surface Engineering and Optoelectronics, Slovenia

In modern small opto-electronic devices like field emitter displays, miniature CRTs, channel photo-multipliers, etc., the vacuum requirements are much more stringent than in conventional electron beam devices. As the pressure should be in the UHV region and the volume is typically a few cm@super 3@, a direct measurement is not feasible and is often estimated on the basis of the expected pumping speed of the getter. The present study was arranged to investigate the pressure in small glass tubes (25 - 50 cm@super 3@) after the conventional pumping and bake-out procedure, just after the activation of Ba getters and during a period of several months. They were equipped by a spinning rotor gauge (SRG) sphere. Two getter sizes were studied: barium (St15/AM/O/9.5 and St15/AM/O/5), both made by SAES. After the evaporation by the prescribed procedure, the pressure did not drop, but increased from p=1x10@super -@@super 5@ mbar up to p=1x10@super -@@super 3@ mbar, showing that the pumping speed was completely suppressed by forming of a non-getterable gas. When the same experiments were repeated inside identical glass bulbs connected with a valve to a quadrupole mass spectrometer, formation of methane was observed. The initial rate just after the activation was Q=10@super -@@super 8@ mbar l CH @sub 4@/s, but even after several hours it was still as high as Q=10@super -@@super 9@ mbar l/s. By switching on the hot filament, methane was pumped by the getter after a precedent cracking procedure. The virtual pumping speed was directly related to the heater power, but independent of the getter area. Therefore, within the cathode warm-up period, methane is "pumped" and does not represent a harmful gaseous contaminant in a small electron beam device with a thermionic cathode.

VST-MoP9 Surface Modification of Chamber Material for Standard Vacuum Pressure Measurement*,* ***M. Tosa****, M. Goto, A. Kasahara, K. Yoshihara,* National Institute for Materials Science, Japan

Main residual gas in a vacuum chamber mainly contains hydrogen molecules in an ultra high vacuum. Reduction of adsorption of hydrogen and other gas molecules is inevitable for standard stable vacuum atmosphere to calibrate standard vacuum pressure g auge. We tried to develop surface modification to reduce adsorption of hydrogen as well as other molecules. Surface modification is developed with surface segregation of hexagonal boron nitride (h-BN) on copper coating film. Copper is excellent in low hyd roge n solution, high thermal conductivity and high vacuum packing but suffers from easy oxidation that becomes large outgassing source. Surface of h-BN is excellent in low gas adsorption but is brittle and preparation of uniform BN layer on the entire sub str ate surface is not easy. Co-sputtering technology using helicon radio frequency wave with a sintered BN disc and a Cu disc deposited mixture of Cu and BN (Cu/B/N) on stainless steel substrates as chamber material. Annealing Cu/B/N film could remove all three main copper spectra peaks with Auger electron spectroscopy, carbon and oxygen peaks largely, then boron and nitrogen peaks increased much higher. Scanning i mage shows perfect uniformity of surface coverage with BN and no element by gas adsorption on the surface after atmospheric exposure. X-ray photoelectron spectroscopy showed @pi@ bond shake-up satellite of boron peak peculiar to h-BN. It is concluded that h-BN segregated uniformly on all the surface of the deposited film. Atomic force microscop e shows that the surface of the segregated h-BN layer has same small value of van der Walls' force as that of a sintered h-BN disc. This concludes that h-BN surface segregation layer on the substrate mixed with BN and copper can weaken surface interaction with gas molecules in a vacuum chamber and can much lower gas adsorption on the surface of the chamber wall for steady standard vacuum atmosphere.

VST-MoP10 Outgassing Rate of Newly Titanium Alloy Material*,* ***H. Kurisu,*** Yamaguchi University, Japan*; M. Hesaka,* Shinko Industrials Co., Japan*; T. Muranaka, S. Yamamoto, M. Matsuura,* Yamaguchi University, Japan

A low outgassing rate material is required to make an XHV system. Titanium is a new candidate material for use in UHV and XHV. Recently vacuum characteristics of titanium materials were investigated and then it was clarified that the outgassing rate of small samples of chemically polished titanium is smaller by a factor of about 1/3 than that of electropolished stainless steel. (M. Minato and Y. Itoh, 1995) In the present work we pay attention to new titanium alloy material (KOBE STEEL,LTD KS100). In this material very flat surface can be obtained by a polishing and the hardness is larger by a factor about 2 than a titanium. We present outgassing property of the polished new titanium alloy in this paper. To measure the out gassing rate of small samples, we prepared the apparatus employing the orifice method with the orifice conductance is about 2.5x10@super -3@m@super 3@/sec (RT, air). In the vacuum system, the vacuum chamber was made of new titanium alloy and the pumping system consists of two turbo molecular pumps. The measurement limit of the outgassing rate is obtained to be 1.6x10@super -11@Pam/sec, when the sample with 160x10@super 3@m@super 2@ area is used, because the pressures of both upper and lower chambers are reached 1x10@super -8@Pa. We prepared the plate samples of polished new titanium alloy materials with the surface roughness of about 1nm. One set of samples consisted of 180 plates with a size of 20x20x1mm (sample area is about 160x10@super 3@m@super 2@). After rough pumping down, samples were kept at 493K and the chamber kept 453K for 48h and then cooled down to room temperature in 48h. Finally out gassing rate was measured. The outgassing rate of the new titanium alloy samples is obtained to be 1.6x10@super -11@Pam/sec, this value is smaller of the order than that of the stainless steel samples under the same measurement condition. On the conference, we will discuss the out gassing property of new titanium alloy materials in details.

VST-MoP11 An Improved Method to Spot-Weld Difficult Junctions*, E. Ferrenz, A. Amare,* ***C.R. Arumainayagam,*** Wellesley College

Recent advances in spot-welding technology such as high frequency direct current (HFDC) inverter welders provide an improved and reproducible method to spot-weld difficult junctions. The importance of removing the oxide layers on metal surfaces, accurately delivering the weld pulse profile, and controlling the force applied to the materials during the welding process are discussed in the context of resistance spot-welding a molybdenum single crystal to a tantalum loop and attaching a tungsten-rhenium thermocouple to the crystal.

VST-MoP12 Estimation of UHV Ball Bearing's Wear by Spectra Analysis of Residual Pressure*, E.A. Deulin,* ***V.V. Gerasimov****, A.G. Peressadko,* Bauman Moscow State Technical University, Russia

The aim of this work is to show correlation between mechanical and vacuum parameters of UHV feedthrough and it's reliability.@footnote 1@ The variation of torque M, outgassing flow in dependence of working cycle's number was investigated. This experiment was carried out on experimental UHV installation with parameters: residual pressure P=7*10@super -5@ Pa, volume of vacuum chamber V=32 l, pumping speed S=150 l/s. The subject of research is a typical ultrahigh vacuum (UHV) mechanism - rotation motion feedthrough. It uses three ball bearings working in UHV. The ball bearings of stainless steel with and without Pb coverage were tested. The analyzed rotary feedthrough was rotating with speed 200 rpm. The diagnosing signals M and Q were storaged every 2000 revolutions of the shaft. The criteria of failure was the achieving by own torque the level of 2 N*m. The correlation level of an average torque M@sub a@, and the maximum torque M@sub max@ parameters with another ones (Q - summarized outgassing flow, Q@sub 1@ - the spectral power of base frequency) was analyzed. The results show that the longevity of feedthrough based on M@sub max@ parameter with ball bearings covered Pb was 170*10@super 3@ of working cycles. The average outgassing flow Q for them was about 1*10@super -4@ torr*l/s. The longevity of feedthrough based on M@sub max@ parameter with ball bearings without coverage was 33*10@super 3@ of working cycles. The average outgassing flow Q for them was about 1*10@super -5@ torr*l/s. During experiment it was shown that the outgassing flow had a periodical charater. The results show that the amplitude of Q@sub 1@ had a good correlation with M@sub max@, that's why we could choose it as one of the main diagnosing parameter. @FootnoteText@ @footnote 1@A.Toy., Control and diagnostics can improve your vacuum, if you know your needs., Semiconductor International., October 1989, pp. 61-63.

VST-MoP14 Surface Cleaning on Aluminum for Ultra-high Vacuum using Supercritical Fluid CO@sub 2@ with O@sub 2@*,* ***T. Momose,*** *H. Iki,* Miyagi National College of Technology, Japan

Contamination on metals used in ultra-high vacuum equipments causes the degradation of function of the equipments. Therefore, cleaning of metal surface is necessary. Supercritical fluid (SCF) carbon dioxide (CO@sub2@)

with high solubility for organic compounds was employed for the cleaning.@footnote 1@ However, the cleaning rate using SCFCO@sub2@ alone was low.@footnote 2@ Therefore, oxygen gas (O@sub2@) was added to SCFCO@sub2@. Aluminum (Al) sample is @phi@5 x t1 mm. Sample was analyzed using x-ray photoelectron spectroscopy (XPS). It is defined that carbon (C) 1s peak in XPS spectra represents contamination. It is also defined that contamination rate is the ratio of area of C1s peak and summation of the area of C1s, O1s, and Al2p peaks. The cleaning rate at 55 °C for 30 minute cleaning was 2 % at 25 mega-Pascal (MPa) in SCFCO@sub2@ without O@sub2@, and 25 % at 20-30 MPa in SCFCO@sub2@ with O@sub2@ of 1.5 MPa. The addition of O@sub2@ is effective on the cleaning using SCFCO@sub2@. Cleaning at the constant ratio of O@sub2@ in SCFCO@sub2@ showed that cleaning rate is approximately proportional to the oxygen molecule number. @FootnoteText@@footnote 1@ H. Mishina, and T. Momose, et.al., J. Vacuum Soc. Japan, 43,No3, 2000, 341. @footnote 2@ T.Momose et.al, JVST, A17(4), Jul/Aug, 1999, 1391.

VST-MoP15 Influence of Ozonized Water Treatment and Subsequent in situ Sputter Cleaning on Electrical Breakdown Characteristics of Oxygen-free Copper Electrodes of a Vacuum Gap*, S. Kobayashi,* *K. Sekikawa,* Saitama University, Japan*; K. Asano,* Akita National College of Technology, Japan*; Y. Saito,* High Energy Accelerator Research Organization, Japan

Electrical breakdown characteristics of a vacuum gap depend on the electrode surface conditions, since the breakdown can be initiated by emission of such particles as electrons, ions, gases or clumps. These particles are emitted from contaminant layers of electrode surfaces. To improve breakdown strength removal of contaminant layers is required. Ozonized water treatment is recognized as the process to make surface clean and passivated. It has been exhibited that ozonized water treated oxygen-free copper electrodes can achieve higher breakdown field (breakdown voltage/gap length) after repetitive breakdowns, while the improvement in the breakdown field at the first voltage application (the first breakdown field) is little.@footnote1@ Electrode suface analysis clarified that the surfaces are slightly contaminated after ozonized water treatment. It was therefore considered that this contamination might cause the first breakdown field stay at the similar level to that for the untreated electrodes. To confirm the effect of the recontamination after ozonized water treatment on the first breakdown field, breakdown fields of electrodes treated with ozonized water alone and treated with ozonized water followed by in situ He ion beam sputter cleaning were compared. Experiments revealed that the additional in situ sputter cleaning is much effective on the improvement in the first breakdown field and the value of the breakdown field achieves 74 MV/m (ozonized water treatment condition : concentration ; 4.8 ppm, treatment hour ; for 60 min), while the value for the electrode treated with ozonized water alone is 69 MV/m. Also revealed is the excellent conditioning effect, that is, after 500 repetitive breakdowns the breakdown field achieves the value of 269 MV/m at 0.3 mm gap length. This value corresponds to the fact that the voltage of about 80 kV can be applied to 0.3 mm gap.. @FootnoteText@ @footnote 1@K. Sekikawa, et al., Applied Surface Science, Vol. 169-170 (2001) pp. 695-699.

Tuesday Morning, October 30, 2001

Applied Surface Analysis
Room 134 - Session AS-TuM

High Spatial Resolution and Imaging

Moderators: H.J. Mathieu, Swiss Federal Institute of Technology, J.-J. Pireaux, Facultés Universitaires Notre-Dame de la Paix, Belgium

8:20am **AS-TuM1 Chemical Specific Imaging and Micro-spectroscopy of Metal/Semiconductor Interfaces***, **M. Kiskinova,*** Sincrotrone Trieste, Italy **INVITED**

Schottky barrier inhomogeneity at metal/semiconductor interfaces has been considered an important factor in explaining the non-ideal behaviour of the Schottky diodes. However, qualitative understanding of the factors controlling the Schottky barrier lateral variations requires a technique capable of probing both the local chemical and structural specifics of the metal/semiconductor interface and the corresponding band bending at the surface. This requirement has partly been met by adding submicrometer lateral resolution (â‰¤ 0.1 Âµm) to the photoelectron spectroscopy, a chemically sensitive method with a probing depth that can be set to be less than 100 Ã… and the Schottky barriers can be determined from the energy shifts of the photoelectron spectra. The access of photoelectron spectromicroscopy to microscopic interface properties will be illustrated by some recent results for metal/GaN interfaces, obtained using the scanning photoelectron microscope at the ELETTRA light source. The investigations were focused on development of chemical heterogeneity at related to the defective structure of the GaN epilayers. Using case studies of technologically important Au, Ni, Ti/GaN contacts lateral variations in the microscopic morphology and their effect on the local Schottky barriers will be presented and discussed. The measured negligible lateral band bending fluctuations despite the differences in the film thickness and chemical composition has been identified as a property of the metal/GaN interfaces, not well understood in the frame of the existing theoretical models. Ë™. sâˆ†âˆ†Ë‡.

9:00am **AS-TuM3 The Combination of a Laboratory X-ray Source with an Energy Filtered Bolt-on PEEM Optics: An Innovative Approach Towards Micro-XPS Instrumentation of the Future***, **M. Merkel**, M. Escher, Th. Kammler, J. Settemeyer,* FOCUS GmbH, Germany*; D. Funnemann, B. Gottschlich,* OMICRON GmbH, Germany*; M. Klais, A. Oelsner, Ch. Ziethen, G. Schönhense,* Johannes Gutenberg Universität, Germany

Due to remarkable advances in micro and nano technology, the need for microscopically resolved spectroscopic information continues to increase. The photoemission electron microscope (PEEM) is capable of delivering, laterally, high-resolution images together with detailed spectroscopic information.@footnote 1@ In combination with laboratory excitation sources in the VUV and X-ray range, it offers a very simple method for chemically analysing sample surfaces. To this end, dispersive filters (e.g. of the hemispherical type) are already being used successfully.@footnote 2@ The use of a retarding field analyser combined with a PEEM is an innovative and versatile attempt to obtain microspectra and/or energy filtered images. We describe the instrumentation and we present results obtained with a bolt-on, state-of-the-art PEEM, combined with a modular imaging, high pass energy filter of the RFA type. The excitation is accomplished using a common monochromatised laboratory bolt-on X-ray source. With this equipment, it is possible to obtain XPS-spectra from sample regions smaller than 1µm with an electron energy range up to more than 1000 eV wide.@footnote 3@ Despite the fact that the PEEM acts as a low-pass filter, one could acquire spectra up to the Fermi cut-off without difficulty. The low intensity of high-energy photoelectrons arising from a low excitation source intensity is crucial for tuning the PEEM optics to the desired kinetic energy. The optimal, electron optical parameters typically deviate strongly from those applying to the threshold regime of the PEEM. We offer a means to optimise the optics regardless of the available intensity of the excitation source. @FootnoteText@ @footnote 1@ H. Ade (Ed.), 'Spectromicroscopy', J. Electron Spectrosc. Relat. Phenom. 84 (1997) @footnote 2@ E. Bauer, J. Electron Spectrosc. Relat. Phenom. 114 -116 (2001) 975-987 . @footnote 3@ M.Merkel et al., Surface Science, to be published.

9:20am **AS-TuM4 High Spatial and Spectral Resolution XPS Analysis of Pseudo-Aluminium Alloy Corrosion Sensors***, **C.J. Blomfield,*** Kratos Analytical Ltd, UK*; S.J. Harris, M.C. Hebbron, C.C. Figgures, L.A. Brimecombe,* British Aerospace, UK

Due to increased aircraft lifetimes and a move towards the use of chrome free protective coatings, corrosion sensors will be used to monitor future aircraft structures. These may be based upon pseudo aluminium alloy structures, which will be used to assess the localised corrosion in the airframe. The paper desribes the analysis of a selection of reference materials and actual corrosion sensors (PLR and Galvanic) following corrosion testing. XPS was used to study the distribution of the corrosion products around the sensor and to identify the composition of the surface of the sensors post testing. A combination of both high spatial resolution XPS imaging and small area XPS analysis were used to analyse to sensors fabricated on high resistance silicon and kapton.

9:40am **AS-TuM5 Correlation of High Spatial Resolution XPS Imaging with Phase Contrast AFM using Classification Methods***, **J.E. Fulghum**, K. Artyushkova, J. Farrar,* Kent State University*; D. Surman,* Kratos Analytical, Inc.*; S. Page,* Kratos Analytical, UK

Understanding the surface morphology of heterogeneous organic samples can require the use of several different imaging, as well as spectroscopic, techniques. Even if the techniques have a comparable field of view, correlating data can be difficult since the imaging methods are likely to have different spatial resolutions, sampling depths, sample preparation requirements, damage mechanisms, and data interpretation considerations. Spatial resolution in laboratory-based XPS imaging instruments is now approaching the sub-micron scale. As the XPS spatial resolution improves, correlations with microscopic techniques such as AFM become potentially possible. We will discuss methods for correlating the chemical information in photoelectron images with the phases identified through phase contrast AFM. Image classification methods can be used to identify and compare components in photoelectron and AFM images. Results for both polymer grids and heterogeneous polymer blends will be discussed. This work has been partially supported by NSF ALCOM (DMR89-20147).

10:00am **AS-TuM6 Progress in Scanning Tunneling Microscopy at Solid / Liquid Interfaces***, **K. Wandelt,*** Universität Bonn, Germany **INVITED**

A newly designed electrochemical scanning tunneling microscope (EC-STM) enables the combination of STM and electrochemical measurements (e.g. cyclic voltammetry) within a realistic volume of liquid (electrolyte). Furthermore three different detection modes with the STM, namely potentiostatic, potentiodynamic and spectroscopic, open the possibility to monitor surface structures, structural transition as well as absolute adsorption sites with subatomic resolution. In this lecture a description of the fully homemade electrochemical STM will be given, and its high in-situ performance will be demonstrated by some selected examples including the atomic structure of anionic adsorbates, the morphological changes of the respective electrode surface, the deposition of metal layers and the growth of molecular films.

10:40am **AS-TuM8 Solvent-Assisted Modification of Polymer Surfaces Using Scanning Force Microscopy***, F. Stevens,* Washington State University, USAS*; **R. Leach**, J.T. Dickinson,* Washington State University

The response of thin polymer films and bulk surfaces to combined stress and solvent is important for applications such as protective barriers (e.g., various wrappings), in controlled drug release from polymer hemispheres, resists for lithography, and nanometer scale surface modification. Over a wide range of normal forces, when a polymer is scanned by SFM in contact mode in a solvent, material is not worn away, but rather the polymer surface expands forming a nanometer scale "bump" at and surrounding the scanned location. Furthermore, for sub-micron scan areas one often observs a series of parallel ridges (moguls) perpendicular to the fast scan direction. Previous reports of the formation of raised material have nearly all been in air, required long times or very high forces to form; little evidence has been presented for the mechanism of formation. We have engaged in a detailed study of protrusion formation and raised ridges using poly(methyl methacrylate) in alcohol based solvents. In addition to scanning in air, we have scanned the polymer surface in four solvents with dramatic differences in response. We have also observed the effects of varying contact force, and the effect of using cantilevers with different force constants. We present evidence that both plastic deformation and tip induced swelling play major roles in the observed polymer surface modification by SFM. The stresses applied by the tip generate tensile forces around the tip that likely increase the quantity of solvent that can enter the surface. We show that adding Rhodamine 6G dye to the solvent provides us with evidence that indeed solvent is going into the polymer. Using fluorescence microscopy we can monitor the uptake of dye as a function of scanning and solvent parameters. This study also shows the possibility of introducing small quantities of a chemical into the polymer surface in a highly localized (nanometer scale) fashion.

11:00am **AS-TuM9 AFM Sample Averaging**, ***M. Hasselblatt,*** University of California at Davis; *E.M. Bradbury,* Los Alamos National Laboratory

Soon after its invention,@footnote 1@ Scanning Tunneling Microscopy (STM) developed into a prominent tool for surface analysis in the physical sciences. A rapid expansion of this type of microscopy beyond the physical sciences was achieved by the Atomic Force Microscope (AFM).@footnote 2@ Both types of Scanning Probe Microscopies (SPMs) yield topographic bitmaps of surface properties. Unfortunately, a rigid analysis of these bitmaps is often neglected in light of the ``beautiful'' images obtained. Here, we present a novel approach to enhance the interpretation of data containing repetitive features. It is based on the combination of linear correlation and bilinear bitmap rotation to average over multiple occurrences of the same feature in one SPM micrograph. Essentially, our procedure is similar to sample averaging in any kind of spectroscopy, or adding images acquired by electron microscopy. It can be used successfully to increase the signal to noise ratio of SPM data and to gain more confidence in data analysis of repetitive features. @FootnoteText@ @footnote 1@ G. Binning, H. Rohrer, Ch. Gerber, and E. Weibel.; Surface studies by scanning tunneling microscopy.; Physical Review Letters, 49(1):57, 1982. @footnote 2@ G. Binning, C.F. Quate, and Ch. Gerber.; Atomic force microscope.; Physical Review Letters, 56(9):930, 1986.

11:20am **AS-TuM10 Study on Modification of Hydrogen Trap Site in Nickel and Stainless Steel Using Atom Probe**, ***T. Yoshimura,*** Hitachi, Ltd., Japan; *Y. Ishikawa,* Yokohama National University, Japan

Hydrogen is a dominant outgassing species from stainless steel vacuum chambers and components in ultra-and extremely high vacuum. Vacuum firing and oxidation are common practice to attain a low out gassing rate. Only a few studies have been taken so far to measure the hydrogen concentration profiles in ultrahigh vacuum materials, stainless steel,@footnote 1@ copper@footnote 2@ and aluminum.@footnote 3@ These studies utilize high energy (MeV order) ion beams to probe for hydrogen. Unfortunately, because of energy spread of ion beam, the depth resolution is limited to be layers than 7.5nm, which is equivalent to the thickness of the surface oxide layers of stainless steel as well as those of aluminum alloys prepared in the controlled atmospheres. Consequently, means of MeV ion beam technique, it is hardly possible to examine the hydrogen concentration depth profile in the surface oxide layers or the oxide-metal interface. Atom probe - field ion microscopy (AP-FIM) is unique among the family of surface analysis techniques in that it examines only the outermost atomic layer of the surface atom-by-atom and depth profiling is possible by means of layer-by-layer evaporation without disturbing the structure underneath. The atom probe has no mass limitations from hydrogen to heavier elements and is equally sensitive to all elements. The present study employs a position sensitive atom probe (PoSAP),@footnote 4@ which is a recent addition to variants of the atom probe and makes three dimensional chemical analysis with single atom sensitivity possible, to examine the hydrogen concentration depth profiles in the surface layers as well as the oxide-metal interface.@footnote 5@ Nickel and aged stainless steel comprising Cr-rich region and Fe-rich region with nanometer size was chosen as a model system for modification of hydrogen trap site. Annealing and oxidation of nickel and stainless steel are carried out as the method to modify the hydrogen trap site. Deuterium was used for this experiment in order to increase the atom probe detection quantity of trapped hydrogen. The number of deuterium trapped in Nickel decreases after annealing, which is a modification of trap site by annealing. Deuterium trapped in the oxide layer and in the oxide-nickel interface has been observed with sufficient resolution to determine the extent of trapping on an atomic scale, which is a modification of trap site by oxidation. No remarkable segregation of deuterium trap site was recognized in the separated ferritic phase of aged duplex stainless steel, because the modulated structure has a match interface. However, after oxidation, the number of trap site decreases and the trap site tends to move to the interface between Cr-rich region and Fe-rich region and the oxide-metal interface. Furthermore it should be noted that clustered trap sites would be observed with the modification treatment of oxidation. @FootnoteText@ @footnote 1@ L. Westerberg and B. Hjorvarsson, Vacuum 47 (1996) 687. @footnote 2@M. W. Ruckman, M. Strongin, W. A. Lanford, and W. C. Turner, J. Vac. Sci. Technol. A13 (1995) 1994. @footnote 3@K. Kanazawa, M. Yanokura, M. Aratani and Akiyama, Vacuum 44 (1993) 7. @footnote 4@A. Cerezo, T. J. Godfrey and G. D. W. Smith, Rev. Sci. Instrum. 59 (1988) 862. @footnote 5@T. Yoshimura and Y. Ishikawa, J. Vac. Technol. A 12(4), (1994) 2544.

Advancing toward Sustainability Topical Conference
Room 111 - Session AT-TuM

Climate Change, Sustainable Energy, and Industry

Moderator: R.L. Bersin, Ulvac Technologies, Inc.

9:00am **AT-TuM3 Plasma Fusion Research and the Technical and Spiritual Challenges of Sustainable Energy**, ***I. Hutchinson,*** MIT Plasma Science and Fusion Center **INVITED**

Plentiful energy for economic production is the basis of the industrial world's material comfort; but the present pattern of fossil fuel consumption can not be sustained even for a few decades longer without major future global environmental impact and probably disaster. Thus energy is perhaps the archetypal challenge to sustainability. Technical solutions to energy needs are vital. Renewables and fission can play important roles. Harnessing thermonuclear fusion, the energy source of the stars, has long been an ideal. It has motivated much of the past half century of plasma physics. Fusion is now at a cross-roads. Plasma science has developed magnetic confinement configurations that appear adequate for producing sustained fusion burn, but a demonstration experiment will be big and expensive, with the economic benefits seeming distant. Every technical solution is double-edged. There is no purely technological fix for energy needs or for most other environmental concerns. Changes in habits of consumption, expectations, population, and values will become essential in a sustainable-energy society. These are ultimately spiritual values. Religious faith is the primary source and sustainer of such values, and provides major teaching resources for guiding individuals and society. It is not sufficient, though, to attempt to manipulate those resources in support of secular objectives, however worthy. Religious teaching has authority only when true to God's call. Society cannot at the same time discount religious values in economic or cultural matters and hope to recruit their help in challenges of sustainability.

9:40am **AT-TuM5 Environment and Industry: An Antithesis or Is There an Acceptable Role of Industry**, ***J. Slanina,*** Netherlands Energy Research Foundation (ECN), Netherlands **INVITED**

Environmental problems vary in scale from very local impact, such as urban air quality to true global impact, as is the case of greenhouse gases. The contribution of industry to these environmental problems is variable, but in many cases very important indeed, as example the large contribution of industry in the emissions and emission reduction of Chloro-Fluoro-Compounds (CFC's) can be mentioned. The need for more sustainable production processes is perceived, but implementation is rather slow due to economic (international competition) and (in the case of developing countries) social reasons. On top of that, the perception is currently in the US that environmental groups and NGO have grossly exaggerated the impact of environmental problems. Crying wolf all the time has surely been damaging regarding a balanced public perception of environmental problems. A high point in this development has been the rejection of the Kyoto protocols by US President Bush. And careful and objective analysis of the situation makes clear that severe environmental problems indeed do exist, and that measures are necessary; Health effects of aerosols, the oxidant problem and climatic change, though perhaps at later time as prophesied will remain important issues. The perceived antithesis between industry and research community and responsible environmental organizations creates an unproductive atmosphere where arguments of both sides are no longer heard and understood. To change this situation, restrain in unwarranted extrapolations by environmental groups and NGO's is necessary, but also the perception by industry that industry must take a proactive role. Some typical European mechanism is called "convenants" where industry and government make a "gentleman's agreement" regarding emission abatement. The actual implementation is then left to industry; government's role is only overall monitoring that the goals are met. This instrument has proven to be quite effective and it indeed puts industry in the necessary pro-active role.

10:20am **AT-TuM7 Atmospheric Aerosols and Their Impact on Climate**, ***U. Baltensperger,*** Paul Scherrer Institute, Switzerland **INVITED**

Atmospheric aerosols originate from either naturally occurring processes or anthropogenic activity. They may influence the climate in two important ways, through direct and indirect effects. Direct effects refer to the scattering and absorption of radiation and their subsequent influence on planetary albedo and the climate system. Indirect effects refer to the increase in available cloud condensation nuclei (CCN) due to an increase in anthropogenic aerosol concentration. This is suspected to increase the cloud droplet number concentration and to decrease the mean diameter of cloud droplets for a constant cloud liquid water content. As a result, the increase in cloud albedo is predicted to influence the Earth's radiation budget. These effects are, however, poorly quantified, and more data are therefore needed for a more accurate modelling of the net effect of climate forcing by anthropogenic changes of the atmospheric composition. The World Meteorological Organization (WMO) has established the Global Atmosphere Watch (GAW) Program in order to ensure long-term measurements in order to detect secular trends and to help closing this gap. Concerning aerosols, the objective of the GAW program is to determine the spatio-temporal distribution of aerosol properties related to climate forcing and air quality up to multi-decadal time scales. Presently, GAW consists of some 20 Global stations, which cover different types of aerosols: Clean and polluted continental, marine, arctic, dust, biomass burning, and free troposphere. An overview will be given on the parameters relevant to the quantification of the aerosol impact on climate, illustrated by examples from a remote site in the Central European Alps.

11:00am **AT-TuM9 The Chemistry of Sulfur in the Background Environment: Impacts on Global Climate***, **A.R. Bandy,*** Drexel University

Sulfur is the only element for which the anthropogenic contributions to the global atmospheric burden is much larger than the contribution of natural sources. Since this dominance of anthropogenic sulfur has occurred mostly in the past century the impacts on global climate also have occurred during the past century. This presentation will focus on the impacts of sulfur chemistry on local and global climate using the large body of work on this subject developed over the past 20 years. Much of this presentation will use results from numerous NASA and NSF airborne field programs flown over the past 10 years. Because these programs used high performance instruments developed in the 1980's, data from them account for most of our present knowledge of chemistry of sulfur in the global atmosphere. Sulfur dioxide will receive special attention because it is the most important sulfur gas of anthropogenic origin. The global distribution of sulfur dioxide will be discussed in detail. Background sulfur dioxide of anthropogenic origin will receive particular attention. Since there are no natural non-volcanic sources of sulfur dioxide we will focus on identifying the origin of sulfur dioxide in the background environment where anthropogenic sources have little impact. Finally we will discuss the physics and chemistry of sulfur in the background environment with special emphasis on how these processes impact local and global climate.

11:20am **AT-TuM10 Surface Composition of Atmospheric Aerosol: Forest Fires, Sea Salt and Asian Dust***, **R.E. Peterson**, B.J. Tyler,* University of Utah

The atmospheric aerosol consists of a complex mixture of organic and inorganic compounds. The aerosol has important effects on human health, visibility, climate, and precipitation chemistry. Past effort has concentrated on the determination of number, size and bulk chemical analysis of these particles. Individual particles vary in properties such as toxicity, light attenuation and hygroscopic behavior which are functions of their shape and three dimensional chemical composition. Our group is involved in a continuing effort to characterize individual particle images and compositions using both SEM and ToF-SIMS. This combination provides information on both bulk and surface chemistry and images of single aerosol particles. This study included size segregated samples (via Al substrates in an 8 stage cascade impactor) and bulk aerosol filter samples (via 47 mm Millipore PTFE filters) from the summer 2000 Montana forest fires, from Hawaiian sea salt, and from an Asian Dust event reaching Salt Lake City, Utah in April 2001. Multivariate statistical analysis was used to extract information from the SIMS images. Images of the particles were separated from the image background, which significantly improved our ability to acquire the composition of individual aerosol particles. Montana forest fire aerosol was predominantly submicron, well within the respirable range (PM2.5), and had a characteristic surface identified as the amides of stearic acid and palmitic acid. Sea salt showed a layered structure of organic compounds on the surface of aqueous NaCl. The Asian Dust event could be clearly distinguished from normal Salt Lake City particulate pollution.

Biomaterials
Room 102 - Session BI+MM-TuM
Biomems & Microdevices

Moderator: W. Knoll, Max-Planck-Institut für Polymerforschung, Germany

8:20am **BI+MM-TuM1 Amplification of Biomolecular Interactions into Optical Signals using Liquid Crystals on Nanostructured Surfaces***, **N.L. Abbott**, J. Brake,* University of Wisconsin **INVITED**

Anisotropic interactions between thermotropic liquid crystals and surfaces typically cause liquid crystals to be "anchored" in one or more orientations near surfaces. In this talk, we report the use of surface anchoring phenomena involving liquid crystals for the imaging of biomolecular recognition events on surfaces. The approach is based on the observation that anisotropic forces acting between a liquid crystal and an appropriately designed surface can be perturbed by the formation of biological complexes on the surface. The change in structure of the liquid crystal near the surface is communicated deep into the bulk liquid crystal because the orientational correlation lengths of liquid crystals are typically large (micrometers). We report the design of surfaces with nanometer-scale topography and patterned surface chemistry such that protein molecules, upon binding to ligands hosted on these surfaces, trigger changes in the orientations of 1-20 micrometer-thick films of supported liquid crystals, thus corresponding to a reorientation of ~100,000-1,000,000 mesogens per protein. Binding-induced changes in the intensity of light transmitted through the liquid crystal are easily seen with the naked eye and can be further amplified by using surfaces designed so that protein-ligand recognition causes twisted nematic liquid crystals to untwist. We also use the average gray-scale brightness of the optical appearance of the supported liquid crystal to construct an optical response curve as a function of the amount of bound protein. This approach to detection of ligand-receptor binding does not require labeling of the analyte, does not require the use of a complex apparatus, provides a spatial resolution of micrometers, and is sufficiently simple that it may find use in rapid, direct-read assays performed away from centralized laboratories.

9:00am **BI+MM-TuM3 Micropatterns of Biomolecules on Silicon Hydride Surfaces***, J. Pipper, U. Fritz, R. Dahint, **M. Grunze**,* University of Heidelberg, Germany

Biochips yield a high potential for technological progress in the fields of diagnostics, drug discovery and nanotechnology. They are usually fabricated by photo- and softlithographic methods, various printing techniques or the use of micro electrodes. Common substrate materials are glass-, silicon oxide- and gold surfaces. A powerful alternative to these approaches is the photochemically initiated attachment of terminally functionalized 1-alkenes onto silicon hydride surfaces accompanied by Si-C single bond formation. Although the high potential use of silicon microstructures for biosensing applications has been postulated for years, it has not been exploited yet due to a lack of functional groups suitable for the coupling of biological species. Problems in surface derivatization occur as a result of unwanted parallel chemical reactions and a possible fragmentation of the organic compounds during illumination. This dilemma has now been overcome by temporarily masking the chemical functionalities with non-photolabile protective groups. The paper reports on the spatially resolved, photochemical modification of planar and porous silicon hydride surfaces for the immobilization of DNA, proteins and cells. In combination with photoactive compounds, the method of light induced surface derivatization can also be transferred to organic materials.

9:40am **BI+MM-TuM5 Nano-Scale Effects on the Interfacial Fluidity of Organic Films***, **R.C. Bell**, M.J. Iedema, K. Wu, J.P. Cowin,* Pacific Northwest National Laboratory

Interfaces cause fluids in nano-scale spaces to behave very differently than in bulk. We are able to spatially resolve this fluidity with 0.1 nm resolution and show how nanometer films of glassy 3-methylpentane (3MP) are much less viscous at the vacuum-interface than at the 3MP-metal interface using ion mobility to probe the spatially varying flow properties. The amorphous 3MP films are constructed using molecular beam epitaxy on a Pt(111) substrate at low temperatures (<30 K). A 1 eV hydronium (D@sub 3@O @super +@) ion beam gently deposits ions on or into the films (the latter by depositing more 3MP on top of the ions). The ion motion is monitored electrostatically as the film is heated at a rate of 0.2 K/s above the bulk glass transition temperature of 3 MP (77 K). However, the ions begin to move at temperatures as low as 40 K near the vacuum interface, well below the bulk glass transition temperature. The viscosity near the vacuum-interface at 80 K is found to be 12 orders of magnitude lower than that ex pected of a bulk film. Furthermore, the fluidity perturbations were found to persist over 2.5 nm, which was determined by precisely placing the ions at increasing distances from the interfaces and monitoring the effect on the ion's mobility. Computer modeling is employed to further extract information about the nature of these films.

10:00am **BI+MM-TuM6 Interfacial BioMEMS: Bridging the Micro to the Macro***, **T. Desai**,* University of Illinois at Chicago **INVITED**

A great deal of consideration has been given in recent years to the biological uses of micro-electro-mechanical systems (MEMS). However, such devices are not yet found in many clinical settings due to lack of appropriate interfacing between these devices and the biological world. This talk will describe approaches to engineer interfaces that enhance the biocompatibility and functionality of implantable MEMS based devices. First, the surface modification of silicon-based devices on the nanometer and micron scale to ensure device functionality and integration will be described. Such chemical modifications must be incorporated onto silicon substrates to modulate the interfacial response, while at the same time ensuring compatibility with microfabrication and micromachining processing. Secondly, microfabrication techniques that can be used to selectively attach and spatially localize chemical species in order to control interfacial reactions with the body will be discussed. By integrating surface modification protocols with MEMS processing, one can create device surfaces that interact appropriately with multiple populations of cells and the surrounding tissue. The identification of principles for engineering microdevice surfaces will aid in developing therapeutic bioMEMS, lab on a chip platforms, and drug delivery systems that can more effectively interface with the biological world.

10:40am **BI+MM-TuM8 Dynamics of Biomolecular Recognition on Calibrated Beads in Microfluidic Channels***, **G.P. Lopez**, T. Buranda, J. Huang,* The University of New Mexico*; V.H. Perez-Luna,* Illinois Institute of Technology*; L.S. Sklar,* The University of New Mexico

We have developed a new approach for the analysis of biomolecular recognition in microfluidic systems. The method is based on real-time detection of biomolecular binding to receptor-bearing microspheres comprising affinity microcolumns. The microcolumn format ensures efficient analyte contact with receptors and rapid mixing. Molecular assemblies on microspheres can be characterized and calibrated using flow cytometric techniques prior to packing. Model assays demonstrated include direct fluorescence methods of quantitatively detecting recognition of model analytes by protein receptors and ligands displayed in well-characterized affinity matrices. We establish a model system for detection of recognition between a monoclonal antibody and the FLAG@super TM@ epitope tag. The assay can detect sub-femtomole quantities of antibody with good signal-to-noise ratio and a large dynamic range spanning nearly four orders of magnitude in analyte concentration. Kinetic and equilibrium constants for the reaction of this receptor-ligand pair are obtained through modeling of kinetic responses of the microcolumn and are consistent with those obtained by flow cytometry. Because of the correlation between kinetic and equilibrium data obtained for the microcolumns, quantitative analysis can be done in minutes, prior to the steady state endpoint of the recognition reaction. The approach has the potential to be generalized to a host of bioaffinity assay methods including analysis of small molecule analytes, protein and nucleic acid complexes, and microsystem-based multi-analyte determinations.

11:00am **BI+MM-TuM9 Microfluidic Patterning of Biopolymer Matrices for Cellular Pattern Integrity***, **W. Tan**, T. Desai,* University of Illinois at Chicago

The ability to design and create biologically relevant patterns via microfluidic patterning on surfaces provides new capabilities for cell biology, the production of biosensors and tissue engineering. However, cellular patterns, defined by microfluidic methods, often lose integrity over time due to cell growth and migration immediately upon removal of the PDMS stamp. In this study, biopolymer matrices were used in conjunction with cellular micropatterning to control cell attachment, growth, and long-term maintenance of these patterns. The incorporation of appropriate matrix materials with microfluidic cell patterning methods results in highly compliant patterns of adherent human endothelial cells (HUVECs) and fibroblasts after several day in vitro. Furthermore, cell type and chemical components in these biopolymer matrices influence the ability of the biopolymer matrices to control cell growth, proliferation and compliance to the patterns. Cell growth and migration in micropatterned biopolymers such as agarose, collagen, collagen-GAG mimics, and collagen-fibronectin are quantitatively measured and compared, and cell-matrix interactions are also examined over time. Results suggest that the use of an appropriate biopolymer matrix helps to control cell growth and maintain pattern integrity for long periods of time. This is essential for conducting stable biological experiments, as well as achieving control over tissue engineering constructs with multiple cell types.

11:20am **BI+MM-TuM10 High Throughput Techniques for Non Invasive Cancer Cell Detection***, W.C. Wilson, L.F. Pardo, X.Z. Yu, **T. Boland**,* Clemson University

The usefulness of patterned surfaces, which specifically bind antagonists has been recognized for a wide variety of biomedical applications ranging from drug screening to tissue engineering. Current technologies for creating patterned surfaces suffer from many drawbacks. For optimized results, technologies that are flexible, use a large number of different proteins, high-throughput and inexpensive are warranted. Ink jet technology has shown promise in meeting these criteria and commercial systems are being developed. High throughput and quantitative assaying of the patterns is equally challenging. For example, in early cancer detection, it is desirable to detect a few abnormal cells within millions of normal cells. It is unlikely that PCR based techniques or gene chips will be economically feasible tools for early detection since most of the cost will be associated with analyzing normal DNA. Economical high-throughput screening and concentration technologies may be able to discriminate and select abnormal cells for further analysis. We developed a piezo driven protein and cell printer in our laboratory, able to simultaneously deposit picoliter drops of cell or protein solutions out of nine nozzles. The printer can deliver a single cell per drop to a surface with submicron resolution. Furthermore, it is equipped with a robotic arm and conveyer belt allowing for truly high-throughput printing. Examples of its use including for anti angiogenesis drug screening will be presented. Quantitative assaying is done using a cell scanner. The cell scanner has a resolution of less than 2 Âµ, is fully computer controlled, high-throughput and an economically attractive when compared to epifluorescent microscopes. Results will be presented with fluorescently labeled cells demonstrating the potential of the cell scanner for high-throughput discrimination and selection of prostate cancer cells.

11:40am **BI+MM-TuM11 Electrochemically-Activated Switching of Surface Chemistry Using Tethered Molecular Machines***, **B.C. Bunker**, D.L. Huber, J.G. Kushmerick, M. Kelly, C.M. Matzke,* Sandia National Laboratories*; J.F. Stoddart, J. Cao, J.O. Jeppesen, J. Perkins,* University of California, Los Angeles

Sandia National Laboratories is integrating "smart" coatings into microanalytical systems for transporting, separating, and detecting species such as proteins. This paper describes the first demonstration of the use of electrochemically-activated molecular machines to switch surface chemistries. The "motor" for the machines being studied consists of an open aromatic ring system (cyclobis(paraquat-p-phenylene)) referred to as the "blue-box" due to its strong optical absorption properties. Reversible oxidation or reduction of the blue box makes it attract or repel aromatic threads such as functionalized naphthalenes or tetrathiafulvalene (TTF). Researchers at UCLA have succeeded in attaching a disulfide-terminated tail to the blue box which is used to tether the blue box to gold surfaces. Ellipsometry and atomic force microscopy measurements indicate that monolayer films of the blue box are produced. Electrochemical measurements indicate that while the voltages required to reduce the blue box are similar to voltages known to induce switching of the box in solution, adsorption of naphthalene threads is irreversible. Reversible switching is only seen for TTF threads that can themselves be oxidized. Contact angle measurements show that reversible changes in surface chemistry can be induced using appropriate threads. A simple microelectronic device has been constructed to demonstrate how the molecular machines can be used to move liquids or dissolved species within microfluidic systems.

Dielectrics

Room 130 - Session DI-TuM

High K Dielectrics II

Moderator: Y. Yasuda, Nagoya University, Japan

8:20am **DI-TuM1 Vibrational and Band-Gap Engineering of Transition Metal Oxides for High-k Gate Applications**, ***S. Zollner***, *R. Liu,* Motorola SPS **INVITED**

CMOS devices will change around 2005, when the SiO2 thickness reaches 15-20 A and the gate length 0.1 um. Beyond that, the physical thickness of the gate oxide can no longer shrink, since the leakage currents due to tunneling render the devices useless. Instead of reducing the physical thickness, scaling the gate length is accompanied by increasing the low-frequency dielectric constant k of the gate oxide. Apart from a number of requirements related to stability under CMOS processing, new gate oxide materials need to have properties that can be engineered by changing the electronic band structure and the vibrational properties: (1) A large band gap with reasonable band offsets compared to the valence and conduction bands of Si. (2) A large lattice polarizability, which can be associated with a soft phonon driving a transition between two crystalline phases. In a way, engineering of the band gaps and band offsets of high-k gate oxides is not too different from band-engineered semiconductors, such as SiGe:C or InGaP for heterostructure bipolar transistors. Optical spectroscopies (spectroscopic ellipsometry from 300 um to 9 eV, FTIR transmission and reflection, UV Raman scattering) and x-ray structural analysis are ideally suited for a rapid screening of a large class of materials for potential high-k applications, since they do not require processing for electrical measurements. Ab initio band structure calculations can assist in the interpretation of experimental results. This talk will describe recent work on SrTiO3 and various transition metal oxides (TiO2, ZrO2, and HfO2). Specifically, we will show how the band gap of SrTiO3 can be increased by 0.5 eV or more through changing the composition, which reduces the leakage currents of metal-gate CMOS devices. @FootnoteText@ Collaborators: R. Gregory, P. Fejes, A. Demkov, J. Curless, Z. Yu, J. Ramdani, R. Droopad, K. Reid, B.-Y. Nguyen, T.E. Tiwald, J.N. Hilfiker, J.A. Woollam.

9:00am **DI-TuM3 Electrical and Physical Characteristics of Sputtered HfO@sub 2@ Films for Alternative Gate Dielectrics**, ***S.-W. Nam***, *J.-H. Yoo, H.-J. Choi, S. Nam, D.-H. Ko,* Yonsei University, Korea*; J.-H. Ku,* R&D Center Semiconductor Samsung Electronics Co., Korea*; M.-H. Cho,* Yonsei University, Korea*; S. Choi,* R&D Center Semiconductor Samsung Electronics Co., Korea*; C.-W. Yang,* Sungkyunkwan University, Korea

SiO@sub 2@ has been used as the primary gate dielectric material in MOSFET devices for over 40 years. As the thickness of SiO@sub 2@ decreases, a direct tunneling of carriers through the potential barrier occurs, which results in the significant leakage current through the SiO@sub 2@ layer. Because of this issue, a conventional SiO@sub 2@ process shows limitation in the fabrication of CMOS devices in sub-2.0nm thickness regime. Therefore, the development of alternative dielectric materials is required for the fabrication of sub-0.1µm MOSFET devices. Dielectric materials with a high dielectric constant, large band-gap, low interface state density, and good thermal stability have drawn a lot of attention as alternative gate dielectric materials. Recently, HfO@sub 2@ has been considered as promising alternative materials due to high dielectric constant and good thermal stability with Si substrates. We have studied the microstructures and electrical properties of HfO@sub 2@ films. The HfO@sub 2@ thin films on (100) silicon substrate treated by a HF solution, chemical oxide, and NH@sub 3@ nitridation were deposited by reactive dc magnetron sputtering for gate dielectrics applications, followed by Pt sputtering for gate electrode. The resulting films were analyzed by ellipsometry, XRD, HRTEM, RBS, and XPS/AES. The crystalline peaks with orthorhombic phase of HfO@sub 2@ were observed in the films annealed at elevated temperatures (>650°C). By HRTEM and XPS/AES analyses, we observed the properties of HfO@sub 2@ films and the interfacial layers between the HfO@sub 2@ films and the Si substrate upon annealing. The electrical properties were assessed by C-V and I-V measurements for MOS structures.

9:40am **DI-TuM5 Solid State Reactions in Hafnium Silicate Thin Films**, *H.T. Johnson-Steigelman, A.V. Brinck,* ***P.F. Lyman,*** University of Wisconsin-Milwaukee

Oxides and silicates of hafnium are promising high-dielectric candidates for microelectronics applications because it seems likely that these materials will be stable at their interface with silicon@footnote 1@ due to the large heat of formation of Hf oxides. If hafnium oxides and silicates are indeed stable against reduction by Si at the dielectric/silicon interface, then, as a corollary, Hf metal should be able to reduce SiO@sub 2@. This supposition was tested by forming nm-thick films of hafnium silicates by solid state reaction of Hf metal films deposited on SiO@sub 2@ in ultrahigh vacuum. Charge transfer during the reaction was monitored by examining the binding energies of the Hf 4f and Si 2p core levels using x-ray photoelectron spectroscopy (XPS). As predicted, the Hf levels shifted to deeper binding energies upon annealing, while the Si core level corresponding to SiO@sub 2@ shifted to shallower binding energy. These shifts are consistent with charge being transferred from the Hf to the Si atoms, as would be expected for reduction of SiO@sub 2@ by Hf. Other aspects of the reaction between Hf, O, and Si were explored using thicker (µm) films. It is clear from these investigations that Hf metal can consume SiO@sub 2@ layers, with sometimes surprising results. @FootnoteText@ @footnote 1@ G.D. Wilk and R.M. Wallace, Appl. Phys. Lett. V.76, p.112 (2000)

10:00am **DI-TuM6 Kinetic Study on ZrO@sub 2@-CVD using Zirconium-Tetra-tertiary-Butoxide**, ***T. Kawamoto***, *Y. Shimogaki,* University of Tokyo, Japan

ZrO@sub 2@ films have lately attracted much attention as high-k dielectrics for high performance ULSI gate applications. We carried out kinetic study on ZrO@sub 2@-CVD by using hot-wall tubular reactor to understand the basic reaction mechanisms. Zirconium-Tetra-tertiary-Butoxide (ZTB) was used as the Zr source and injected into the reactor by bubbling with He. We investigated the fractured surface of the sample by FE-SEM to obtain the growth-rate and step coverage of deposited ZrO@sub 2@ films on Si substrate with microtrenches. The deposition profile at 663K showed the increase in the up-stream part, and then the decrease was observed in the down-stream part. This implies that this reactive process has the special path, precursors decomposed into intermediate species by the gas-phase reaction, and the intermediate species deposits on growing surface. Furthermore, we examined depositions into the trench substrates with different aspect ratio at several positions in the reactor, and could found out that the step coverage became poorer, as samples were laid further from inlet. As a result of carrying out fitting these experimentally observed step coverage profiles with a single species model, the predicted composition profiles did not match well with the all observed profiles. This result indicates that some growth species contribute to film growth. Then, by fitting with two species model, we determined reactive sticking coefficients of two growth species; @eta@@sub 1@=0.0095 and @eta@@sub 2@=0.20, respectively. And we found out that the less active growth species (@eta@@sub 1@=0.0095) existed dominantly in the up-stream part, on the other hand, the high active growth species (@eta@@sub 2@=0.20) did the same role in the down-stream part. The dependence of the step coverage quality on the distance from inlet could be explained by the relative ratio of these species. The film properties may have different characteristics by this precursor ratio.

10:40am **DI-TuM8 Correlations Between Local Bonding and Electronic Structure, and Gate Dielectric Performance of Zirconium Silicate Alloys**, ***G. Rayner, Jr.***, *D. Kang, M. Schultz, G. Appel, G. Lucovsky, H. Ade, D.E. Aspnes, D.E. Sayers,* North Carolina State University

Zirconium silicate alloys have been prepared by remote plasma enhanced metal organic chemical vapor deposition, RPE-MOCVD, using down-stream injected SiH@sub 4@ as the Si-atom source, Zr(IV) t-butoxide as the Zr-atom source, and plasma excited O@sub 2@/He mixtures to produce active oxygen species to drive the deposition reactions. Bulk film properties have been studied for as-deposited films, and films subjected to post-deposition annealing at temperatures to 1000C in an Ar ambient. This paper extends previously reported studies of thermal stability (chemical phase separation and crystallization) by infrared, IR, spectroscopy and x-ray diffraction, XRD.@footnote 1@ Specific spectroscopic studies include i) x-ray photoelectron spectroscopy, XPS, ii) x-ray absorption spectroscopy, XAS, iii) extended x-ray absorption fine structure, EXAFS, and iv) spectroscopic ellipsometry, SE. The spectroscopic studies have confirmed that the lowest lying anti-bonding states are derived from d-states of the Zr-atoms. Results demonstrate that the energy of these states relative to vacuum, and the Si conduction band, do not change as a function of alloying, or as a function of long or short range order. This result is consistent with a molecular orbital description of the electronic structure derived from the Zr d-states. This aspect of the electronic structure has important implications for the interpretation of electrical studies, e.g., current-voltage and capacitance-voltage measurements that are also reported in this talk. For example, changes in the coordination and bonding symmetry of the bonding and anti-bonding orbitals derived from Zr d-states provide insights into the microscopic mechanism responsible for enhancements in the dielectric constant at low ZrO@sub 2@ concentrations.@footnote 2@ Supported by ONR, SRC and the Sematech SRC Center for Front End Processes @FootnoteText@ @footnote 1@ G. Rayner, R. Therrien and G. Lucovsky, MRS Symp Proc 611, c1 3.1 (2001) @footnote 2@ G. Lucovsky and G. Rayner, Appl. Phys. Lett. 77, 2912 (2000).

11:20am **DI-TuM10 Interface Reactions of High-K Y@sub 2@O@sub 3@ and Gd@sub 2@O@sub 3@ Gate Oxides with Si***, B.W. Busch,* Agere Systems*; W.H. Schulte,* Rutgers University*; R. Kwo, M. Hong, J.P. Mannaerts, B.J. Sapjeta,* Agere Systems*; T. Gustafsson, **E. Garfunkel**,* Rutgers University

Ultrathin Y2O3 and Gd2O3 films were e-beam evaporated onto Si(100) and investigated by high-resolution medium energy ion scattering with and without in-situ Si capping layers. Si-capped metal oxide films were stoichiometric (M2O3), and their interface with the Si substrate was sharp. Uncapped films that were exposed to air, however, contained excess oxygen and showed a 6-8 @Ao@ thick interfacial layer. Other than limited intermixing between the capping Si and metal oxide layers during deposition, the oxides did not react with the initially-amorphous Si overlayer until ~800 °C. Uncapped films showed additional Si uptake from the substrate at ~700 °C, while the capped films did not react with the substrate until ~900 °C. Results are discussed within the framework of the relevant solid-solid and solid-gas thermodynamics and kinetics. This work demonstrates the critical importance of gas ambient during growth and processing of high-K gate oxides.

Magnetic Interfaces and Nanostructures
Room 110 - Session MI+EL-TuM

Spintronics I: Magnetization Dynamics and New Materials

Moderator: S.E. Russek, National Institute of Standards and Technology

8:20am **MI+EL-TuM1 Noise-Derived Anisotropy Energy Distributions of Cobalt Nanoparticle Films***, **S.I. Woods**, R.H. Koch, S. Sun, J. Kirtley,* IBM T.J. Watson Research Center **INVITED**

9:00am **MI+EL-TuM3 Spin Wave Dynamics of Interacting and Non-interacting Magnetic Elements on the Sub-micrometer Scale***, **S.O. Demokritov**, J. Jorzick, B. Hillebrands,* University Kaiserslautern, Germany*; M. Bailleul, C. Fermon,* CEA Saclay, France*; K. Guslienko, A.N. Slavin,* Oakland University*; D. Berkov,* Innovent Jena, Germany

Confinement caused by the lateral edges of small magnetic elements qualitatively changes dynamic properties of such elements. Instead of well-known spin wave bands, characteristic for thin magnetic films that are infinite in plane, one observes quantized spin wave modes with wavevectors determined by the element lateral sizes.@footnote 1@ Here we report a new highly localized spin wave mode in small magnetic elements. This mode was observed using Brillouin light scattering from thermal spin fluctuation in arrays of micrometer-size, 35 nm thick permalloy elements: rectangular dots and stripes magnetized perpendicular to their axes. The in-plane field 0.3-0.6 kOe was high enough to remove the remanence domains in the investigated elements. However, due to the non-elliptical shape of the elements the total saturation cannot be reached at any applied field. Domains (near the edges of the element that are perpendicular to the field) exist. The observed new mode is localized near those edge domains and has a frequency of 4-6 GHz depending on the applied field. The width of the localization region is much smaller than the lateral size of the element (< 200 nm). Due to high magnetic susceptibility in the region of the mode localization the mode amplitude caused by thermal fluctuation is much higher than that of the quantized modes. The experimental observation of a new mode is confirmed by a theoretical analysis, based on the solution of a non-local dipole problem, as well as by numerical simulations. If the distance between the elements in an array approaches a value comparable with their thickness, the dipole-dipole interaction between the elements becomes measurable. Due to this interaction the phase locking of the spin waves of neighboring elements takes place: spin fluctuations in different elements are correlated. Thus, a collective spin wave mode propagating through the array of magnetic elements is created. @FootnoteText@@footnote 1@J. Jorzick et al. Phys. Rev. B, 60 (1999) 15194.

9:40am **MI+EL-TuM5 In-situ Characterization of Spin-dependent Scattering Mechanisms in GMR Spin Valves***, **W.E. Bailey**, S.E. Russek,* NIST, Boulder **INVITED**

Although giant magnetoresistance (GMR) is widely used in magnetic recording, the relative importance of electronic scattering locations which contribute to--or limit--the effect is not generally agreed upon. The technologically important case of the Co/Cu/Co "spin-valve" trilayer is particularly rich since questions of surface scattering and possible channeling effects in the current-in-plane geometry (CIP-GMR) may be considered along with older questions of bulk vs. interface spin-dependent scattering. The role of surface scattering is crucial since it is widely believed that its reduction, through specularity enhancement, could provide a three- to tenfold enhancement of the spin-valve GMR. We have developed the in-situ magnetoresistance measurement as a method to locate scattering centers in the spin valve and to provide additional information on their nature. Film conductance and GMR are measured in-situ, in UHV, and in real time during magnetron sputtering, allowing the effects of interfaces and surfaces on scattering to be identified as they are created. Results from two sets of experiments will be presented. First, the onset of GMR has been investigated in NiO/Co(30)/Cu(30 Å)/Co(t) spin valves with ultrathin free layers. A main contribution to GMR is attributable to the interface alone, with a conductance response suggestive of the formation of a channeling state. Second, the response of GMR to surface treatment has been measured during coverage of NiO/Co(30)/Cu(30 Å)/Co(t) spin valves with noble metals and nano-oxide layers ("NOL"). The results in these cases do not match well with simple models of surface diffuse scattering or its reduction, and may be incompatible with them.

10:20am **MI+EL-TuM7 Highly Spin-Polarized Materials***, **C.L. Chien**,* Johns Hopkins University **INVITED**

Magnetic heterostructures of highly spin polarized materials provide opportunities for the exploration of new physical phenomena and the development of spintronic devices where both charge and spin of electrons are exploited. Materials with spin polarizat ion (P) higher than those of traditional ferromagnets (P < 45% for Fe, Co, and Ni), and especially half-metallic ferromagnets with P = 100%, are highly desirable. We describe the measurements of the intrinsic spin polarization of half-metallic CrO2 with P = 96% and the unique magnetic and other electronic properties of these single-crystal CrO2 films, epitaxially grown on TiO2 substrates by chemical vapor deposition.

11:00am **MI+EL-TuM9 Characterization of a New Half-Metallic Ferromagnet: Yb@sub 14@MnSb@sub 11@***, **A.P. Holm**, S.M. Kauzlarich,* University of California, Davis*; S.A. Morton, G.D. Waddill,* University of Missouri-Rolla*; W.E. Pickett,* University of California, Davis*; J.G. Tobin,* Lawrence Livermore National Laboratory

Utilizing a combination of bulk magnetization and magnetic X-ray circular dichroism measurements (MXCD), we demonstrate that Yb@sub 14@MnSb@sub 11@ is a half-metallic ferromagnet. The compound is isostructural to Ca@sub 14@AlSb@sub 11@, with the Mn occupying the Al site in the [AlSb@sub 4@]@sup 9-@ discrete tetrahedral, anionic unit. Bulk magnetization measurements exhibit an effective moment of 4.86 ± 0.02 µ@sub B@/ formula unit implying a Mn@sup 3+@, high spin d@sup 4@ state, but theoretical calculations suggest Mn is divalent with one hole in the Sb 5p states of the tetrahedron. MXCD measurements reveal that the Mn L@sub 23@ is strongly dichroic, and there is no evidence of any dichroism in either the Yb N@sub 45@ or Sb M@sub 45@ edges. Comparisons of the Mn spectra with the theoretical models for Mn@sup 2+@ show excellent agreement, and support the bulk magnetization measurements. The bulk magnetization measurements clearly show full spin alignment and the cancellation of one spin by the unpaired and antialigned spin in the Sb 5p band.

Manufacturing Science and Technology
Room 131 - Session MS-TuM

Process Integration and Factory Productivity

Moderator: S.S. Shankar, Intel Corporation

8:20am **MS-TuM1 Reduction in Loadlock Vent Time and Particles through Use of Fast Vent Diffuser**, *C. Adcock,* Mykrolis Corporation (Formerly the Microelectronics Division of Millipore Corporation)*; H. Dang,* Texas Instruments Inc.*; J. Gratz, M. Randolph,* ***J. Snow****, C. Tsourides,* Mykrolis Corporation*; R. Wheeler,* Millipore Corporation

Improvements to semiconductor manufacturing equipment effectiveness can be directly impacted by enhancements in tool throughput and/or product yield. One area for these improvements is system loadlocks. Reducing loadlock vent-up time from vacuum to atmospheric pressure increases tool throughput. Additionally, reducing particle adders in the loadlock increases product yield. Traditionally, a soft vent procedure has been used in an attempt to balance loadlock vent-up time with reduced particle generation. While some particle control is achieved, vent-up times are often in excess of ten minutes - not an optimal solution. Gas diffuser technology has been developed and integrated with filtration technology to enable faster vent-up of loadlocks while simultaneously decreasing particle adders on the wafer. This is accomplished using a "specially formulated" sintered porous metal membrane, which provides laminar flow across the entire diffuser surface. Vent gas volume is maximized while gas velocity at the loadlock entrance is minimized. Results from two independent evaluations with diffusers will be presented. First, tests conducted at an equipment manufacturer will demonstrate an 80% reduction in vent time with no adverse effect on particle performance. Second, on-tool performance at a semiconductor manufacturing facility will highlight the reduction in wafer particle adders.

8:40am **MS-TuM2 Cleaning Procedures in Wafer Processing: Analytical Challenges for Root Cause Determination of Particle Problems**, ***C.C. Wang****, Y.S. Uritsky, C.R. Brundle,* Applied Materials, Inc.

Common dry clean procedures used in the wafer processing industry are: substrate pre-clean of individual wafer prior to deposition (gentle Ar@super +@ sputter), and hardware clean after many processed wafers to remove the sputtered material build-up (harsh NF@sub 3@ usually). Particle failures can result from both procedures, however, and are a severe industry problem. In the Ar@super +@ pre-clean a gradual build-up of by-products of cleaning occurs on chamber surfaces. These can chemically react with the hardware material, releasing composite particles through stress (proven by detailed particle morphology observation). In the NF@sub 3@ case, the fluorine radicals, intended for removing deposits by forming volatile products, often attack hardware itself producing particles. In both cases particle analysis is critically needed to determine exactly what piece of hardware is being attacked and by what mechanism for the purpose of hardware and process improvements. The sophistication of the analytical work required for finding root cause is high. In this paper we describe how careful SEM/EDX work, supported by FIB and Raman/Photoluminescence, identified root cause in both NF@sub 3@ and Ar@super +@ clean particle failures. In the NF@sub 3@ case the critical issue was to establish, without any doubt, that generated particles scavenged by an oxide monitor wafer, contained no oxygen and only Al and F. In the Ar@super +@ pre-clean case it was demonstrated that particles consisted of thin, plate-like bi-layers of sputtered substrate material (SiON in this case) and amorphous Al@sub 2@O@sub 3@ from the surface of the plasma degraded ceramic dome. In both cases modeling the EDX spectra using STRATAGEM@footnote 1@ software for multi-layer thin film structures (and here applied to particles) was important in reaching definitive conclusions, which were then used in the successful defect reduction actions. @FootnoteText@ @footnote 1@ STRATAGEM is a registered trademark of SAMx.

9:00am **MS-TuM3 High Productivity Plasma Etch Reactors: Hardware and Chemistry Concepts**, ***D. Podlesnik,*** Applied Materials **INVITED**

9:40am **MS-TuM5 Data Driven Manufacturing**, ***C.J. Spanos,*** University of California, Berkeley **INVITED**

Manufacturing has evolved through several stages: From handmade parts, to interchangeable components, from scientific management and statistical process control to numerical control, and finally to intelligent machine tools and flexible production facilities. While it took over 200 years for traditional manufacturing to mature, semiconductor manufacturing advanced through all these stages in four short decades. More so than in other types of manufacturing, today's semiconductor manufacturing is "data driven" in many levels of abstraction. Much like traditional manufacturing, there is tremendous data infrastructure at the factory level, monitoring parts movement, recipes, consumables, etc. Unlike traditional manufacturing, however, there is also data driving the production at the process or tool level. Examples here include the sophisticated control and diagnosis databases that often describe individual process steps of critical nature, such as plasma etching, photolithography and Chemical-Mechanical Planarization. An additional example of unusual datasets in semiconductor manufacturing has to do with the large amount of wafer or work-piece data, collected to monitor tooling, to predict yield, to drive control applications, and to also drive the evolution of semiconductor manufacturing technology. This talk will examine this hierarchy of data in semiconductor manufacturing, and it will specifically focus on the interactions between the various levels. Examples will be given regarding critical deep sub-micron patterning steps of the semiconductor manufacturing sequence.

10:40am **MS-TuM8 Gate Module Integration with High k Dielectrics**, ***S.W. Butler,*** Texas Instruments **INVITED**

Due to silicon dioxide being unable to meet future gate dielectric thickness and leakage requirements, silicon dioxide as a gate dielectric is being replaced with a higher k material, such as a metal silicate. Switching from silicon dioxide to a higher k dielectric involves more than just changing the dielectric. Although the goal is to minimize changes to a traditional CMOS flow, this paper will discuss the reality of the types of changes that must be made for the transistor to achieve improved performance and meet the SIA Roadmap requirements. Temperature changes are the most common type of change considered. However, there are more subtle process and flow changes which can be quite insidious and their impact must be understood. Contamination concerns may also drive process changes, but are more likely to cause procedural or manufacturing system changes. Such changes may be considered more expensive by a production fab than a process or equipment change.

Nanotubes: Science and Applications Topical Conference
Room 133 - Session NT+EL+NS-TuM

Nanotubes: Growth and Characterization

Moderator: S.B. Sinnott, The University of Florida

8:20am **NT+EL+NS-TuM1 Modification of Single wall Carbon Nanotubes**, ***S. Iijima,*** NEC Corporation, JST-ICORP and Meijo University, Japan **INVITED**

This talk will discuss hybrid structures of SWNTS with other materials such as various types of fullerenes and other molecules which are incorporated into the interior spaces of nanotubes. It will also cover discussion on chemical modification of SWNTs with organic materials.

9:00am **NT+EL+NS-TuM3 Patterned Growth of Vertically Aligned Carbon Nanofibers by High Density Plasma Enhanced Chemical Vapor Deposition**, ***J.B.O. Caughman****, V.I. Merkulov, D.H. Lowndes, E.D. Ellis, L.R. Baylor, M.A. Guillorn,* Oak Ridge National Laboratory

Vertically aligned carbon nanofibers (VACNFs) are being studied for use as field emitters. The VACNFs have been grown on a nickel catalyst layer using a high density inductively coupled plasma source. The source operates at 13.56 MHz and couples power to the plasma via a flat spiral coil. A hydrogen and acetylene plasma is used to produce the precursors needed for growth. The aligned VACNFs are grown on a heated substrate located downstream from the ionization zone. The energy of the ions impacting the growth surface is controlled with radio frequency bias. Self-bias voltages are typically in the range of -50 to -300 V. Operating pressures are in the range of 50 to 200 mTorr and growth temperature is typically around 700 degrees C. Results show that the diameter of the VACNFs depends on the size of the nickel catalyst particle and are typically 25-100 nm in diameter. The height of the VACNFs depends on the growth time and bias conditions, with typical lengths of around 1 micron. The VACNFs have been grown on nickel patterns on silicon to form arrays of isolated emitters. The relationship between growth conditions and field emission will be presented.@footnote 1@ @FootnoteText@ @footnote 1@ Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Dept. of Energy under contract DE-AC05-00OR22725.

9:20am **NT+EL+NS-TuM4 Large-Area Growth of Well-Aligned Carbon Nanotubes by Hot-Filament-Assisted DC Plasma Chemical Vapor Deposition***, **T. Negishi**, Y. Hayashi, S. Nishino,* Kyoto Institute of Technology, Japan

For the realization of field emission displays (FED) using carbon nanotubes (CNT), the efficient production method of CNT suitable for them should be developed. In order to obtain aligned CNT perpendicular to substrates for the application, direct growth on catalyst metal plates is desirable. It was reported that well-aligned carbon nanotubes were grown by plasma chemical vapor deposition (CVD). However the growth area was less than 1 inch in diameter. We have succeeded in carrying out the growth of well-aligned CNT with high density on a 5 cm x 5 cm nickel plate by hot-filament-assisted DC plasma (HF-DCP) CVD in the gas of CH@sub 4@/H@sub 2@. The growth method and conditions were as follow. DC voltage of -500V was impressed on the substrate with hot-filaments grounded. The filaments not only raise the temperature of a substrate, but stabilize a DC plasma. A luminous region was observed just above the substrate. By the optical emission spectroscopy, it was confirmed that the luminescence was derived from exited hydrogen and hydrocarbon radicals. Therefore the process is called HF-DCP CVD. Nickel substrates were heated by the filaments to 450-600 °C. The substrates were pretreated in pure hydrogen plasma before the growth of carbon nanotubes. Well-algined CNT about 50 nm in diameter and about 10 microns in length were observed by scanning electron microscopy in the density of about 10@super 9@ cm@super -2@ on the surface of the treated substrate. Field-emission properties of CNT were evaluated and a current density of 1.2 mA/cm@super 2@ was obtained for -1500V bias between the substrate and the counter electrode with a distance of 300 um. By this method, the growth of well-aligned CNT in an even larger area is expected.

9:40am **NT+EL+NS-TuM5 Tailoring Growth and Properties of Nanotube Networks for Applications***, **B.-Q. Wei**, Y.-P. Zhao, P.M. Ajayan, G. Ramanath,* Rensselaer Polytechnic Institute

We present strategies for obtaining aligned nanotube architectures, and locally modifying their nanotube properties, to enable their use for applications such as interconnects in future devices. We demonstrate various methodologies such as substrate templating, using gas-phase catalysts delivery, and interfacial reactions, to obtain substrate-selective growth, vertical as well as horizontal alignment, and metal-nanotube-substrate connection formation by chemical vapor deposition (CVD). We describe the use of focused ion beam (FIB) to modify the nanotube structure after deposition. We show that by controlling ion energy and dose, one can either tailor the electrical properties of nanotubes and/or micromachine them. We also report, for the first time, a nanotube-length-independent piezoelectric-like resonance in the impedance spectrum at ~ 37.6 kHz during AC probing of single-walled nanotubes. These will be relevant from the viewpoint of building devices such as ultrasonic nanotransducers, quantum well devices and nano-electromechanical actuators.

10:00am **NT+EL+NS-TuM6 Growth of Carbon Nanotubes and Applications in Microscopy***, **L. Delzeit**, C. Nguyen, R. Stevens, B. Chen, J. Han, M. Meyyappan,* NASA Ames Research Center **INVITED**

11:20am **NT+EL+NS-TuM10 The Effect of Photon Energy, Average Power, and Repetition Rate on Nanotube Synthesis Using a Free Electron Laser***, **B.C. Holloway**, A.D. Friedman,* College of William & Mary*; M.W. Smith,* NASA Langley Research Center*; C.K.W. Adu, A.L. Loper, B.K. Pradham, G. Chen, S. Bhattacharyya, P.C. Eklund,* Pennsylvania State University*; J.E. Fisher,* University of Pennsylvania

The free electron laser (FEL) located at Thomas Jefferson National Accelerator Facility (Jlab) was used to produce single-walled carbon nanotubes (SWNTs) by laser vaporization of a catalyzed carbon target. The Jlab FEL offers the advantage of a high power (~1000 Watts maximum average power), tunable (~2-7 micron), high repetition rate (MHz) photon source where parameters can be varied rather easily compared to tabletop systems. Initial experiments with the FEL show that, under the appropriate conditions, large soot generation rates (>10 mg/min) with high SWNT yield are possible . In addition raman scattering and high resolution transmission electron microscopy (HRTEM) of the FEL-produced material shows novel properties such as larger tube diameters, smaller bundle sizes, and interesting variations with carbon target catalyst composition. While the FEL operating conditions and synthesis system design have not yet been optimized, the potential for large scale production of SWNTS and/or "diameter tuning" using an FEL will also be discussed. Work supported by DARPA, ARO, NSF, and NASA.

11:40am **NT+EL+NS-TuM11 Energy-Filtered Reflection High-Energy Electron Diffraction from Carbon Nanotubes***, **J.T. Drotar**, B.-Q. Wei, Y.-P. Zhao, G. Ramanath, P.M. Ajayan, T.-M. Lu, G.-C. Wang,* Rensselaer Polytechnic Institute

Using reflection high-energy electron diffraction (RHEED), we have observed energy-filtered diffraction patterns from both vertically aligned and randomly oriented multi-walled carbon nanotube samples. The diffraction patterns show a ring structure that roughly corresponds to powder diffraction from graphite. Using a simple kinematic treatment, we were able to obtain information on the crystal structure of the individual nanotubes from the radial profiles of the rings. The interlayer spacing is significantly higher than in graphite, and there is almost no evidence of interlayer correlation. This is consistent with previous x-ray diffraction studies of multi-walled carbon nanotubes. We were also able to obtain information on the alignment and spacing of nanotubes. For the vertically aligned sample, the center to center spacing of the nanotubes was found, from reflection electron energy-loss spectra (REELS), to be 52 ± 12 nm. To the best of our knowledge, this study constitutes the first observation of RHEED patterns from multi-walled nanotubes. @FootnoteText@ This work was supported by NSF and the Interconnects Focus Center New York.

Plasma Science
Room 103 - Session PS1-TuM
Diagnostics II

Moderator: V.M. Donnelly, Agere Systems

8:20am **PS1-TuM1 Radical Concentrations and Temperatures in a Dual-Frequency Capacitive Reactor Determined By Broad-Band UV-Visible Absorption Spectroscopy***, **J. Luque**, E.A. Hudson,* Lam Research*; J.P. Booth,* Ecole Polytechnique, France

Broad-band UV-visible absorption spectroscopy is next in simplicity to optical emission spectroscopy. Unlike optical emission, it provides direct information about ground states of neutral species in plasma environments. However, it has rarely been implemented as diagnostic in industrial plasma reactors. In the present work, we report measurements in a Lam dielectric etch reactor (27/2 MHz dual frequency capacitive) during semiconductor processing using Ar/C@sub x@F@sub y@/O@sub 2@ feedstock gas mixtures. Using a deuterium lamp source and a photodiode array detector we can measure absorption across the 200-260 nm region, allowing simultaneous detection of CF, CF@sub 2@ and SiF@sub 2@ radicals. Other species that we have detected include C@sub 2@ and C@sub 3@. We use the CF radical as example of this technique, and to illustrate the wealth of information easily extracted from moderately high resolution absorption spectra: CF radical ground state number densities are determined with a detection limit of ~10@super 10@ cm@super –3@ using off-the-shelf instrumentation. Typical densities are in the order of 10@super 13@ cm@super –3@ for a standard oxide etch recipe. CF rotational and vibrational temperatures are measured aided by spectral computer simulation code. Typical rotational temperatures, which are normally equivalent to gas temperature in the reactor, are in the order of 425 K. Vibrational distributions, with temperatures of 800 K, show non-thermalization compared to rotational temperatures. We found a previously unreported vibrational band, assigned as CF A-X(3,0), and it is heavily predissociated. Intensities of the CF A-X(v,0) and B-X(v,0) bands are used to determine accurate transition probabilities, enabling precise determination of concentrations and temperatures in future spectroscopic experiments via the CF A-X and B-X bands.

8:40am **PS1-TuM2 CF@sub x@ Kinetics, Gas Temperatures and Instabilities in a CF@sub 4@ Inductively-coupled Discharge***, **J.P. Booth**, H. Abada, P. Chabert,* Ecole Polytechnique, France*; G. Cunge,* CNRS/LETI, France

The use of inductive discharges in fluorocarbon gases for SiO@sub 2@ etch applications has been hampered by narrow process windows and severe process drift problems, despite promising etch rate, selectivity and anisotropy results. We have extended our study of free radical kinetics in capacitively-coupled plasmas to these systems in order to investigate the origin of these problems. Laser-induced fluorescence was used to probe the axial concentration and temperature profiles and the kinetics of CF and CF@sub 2@ radicals in a pure CF@sub 4@ ICP. Rotationally-resolved LIF of CF shows that very high gas temperatures can occur (up to 1000K).

Therefore, large gas temperature and density gradients exist within the reactor. The CF and CF@sub 2@ axial concentration profiles are hollow, showing that these species are produced at the reactor surfaces due to C@sub x@F@sub y@@super +@ ion bombardment, and are destroyed in the gas phase. The nature of the gas-phase destruction processes will be discussed, in relation to the formation of heavier C@sub x@F@sub y@ species. We also observed the occurrence of plasma instabilities over a wide range of gas pressure and injected RF power. This phenomena can mostly be explained in terms of relaxation oscillations between capacitive and inductive plasma modes as observed by previous workers in SF@sub 6@ plasmas, but with the added mechanism of the formation of heavy C@sub x@F@sub y@ oligomers, which are much more electronegative than the parent gas, CF@sub 4@.

9:00am **PS1-TuM3 Time-Resolved CF@sub 2@ Rotational Temperature Measurements in Inductively-Coupled Pulsed Plasmas***, X. Wu,* ***T.M. Bauer,*** University of New Mexico*; J.L. Cecchi,* University of New Mexico, US

We have measured the time evolution of the rotational temperature of CF@sub 2@ in pulsed plasmas. These measurements were performed in an inductively coupled plasma (ICP) reactor with a CHF@sub 3@/Ar gas mixture. We have explored a range of ICP powers of 300 to 900 W and a range of total pressure from 10 to 30 mTorr. The rotational temperature of CF@sub 2@ was determined from absorbance measurements, using a wavelength-modulated diode laser spectroscopy system, modified to provide data with a time resolution of less than 0.1 ms. The @nu@1 band @super R@Q@sub 8@ of CF@sub 2@ eo<->oe and ee<->oo rotational lines J=16, 18, 19, 21-23 are used for analysis. >From the dependence of the line intensities on the energy of the lower state, we are able to extract the rotational temperature. Pulse frequency was varied from 4 to 20 Hz at duty factors from 10 to 50%. The CF@sub 2@ rotational temperature time evolution is characterized by a first order rise upon plasma ignition to a temperature that coincides with the steady state rotational temperature, providing the plasma-on time exceeds the heating time constant, which is typically in the range of 2-5 ms. Once the plasma is extinguished, rotational temperature shows first order decay to about 290 ± 20K. The time constant for this decay is in the range of 5-10 ms.

9:20am **PS1-TuM4 Measurements of H atom and CF@sub x@ Radical Densities in High-density CHF@sub 3@ Plasmas by Laser-induced Fluorescence***,* ***K. Sasaki****, M. Okamoto, K. Kadota,* Nagoya University, Japan

CHF@sub 3@ plasmas are widely used for dry etching of SiO@sub 2@. There are many reports on the diagnostics of CF@sub x@ radicals in CHF@sub 3@ plasmas. However, reliable diagnostics of H atoms in CHF@sub 3@ plasmas have not ever been carried out. H atoms play an important role in scavenging F atoms which obstruct selective etching of SiO@sub 2@. In addition, excess H atoms may results in the damage of Si. Accordingly, the reliable diagnostics of H atoms in CHF@sub 3@ plasmas is an important issue. In the present work, we measured the absolute H atom density in high-density CHF@sub 3@ plasmas by (2+1)-photon laser-induced fluorescence spectroscopy.@footnote 1@ In addition, the absolute densities of CF and CF@sub 2@ radicals were also measured by laser-induced fluorescence. The experiments were carried out in a linear machine with a uniform magnetic field of 1 kG. Helicon-wave discharges were obtained by applying various rf powers to a helical antenna wound around a glass tube of 3 cm diameter. Since the plasma was confined radially by the external magnetic field, we had a slender plasma column with a diameter of 3 cm at the center of the cylindrical vacuum chamber. The H atom density was mainly on the order of 10@super 13@ cm@super -3@ at a CHF@sub 3@ gas pressure of 5 mTorr. The H atom density increased with the electron density of the plasma. Contrary to the H atom density, the CF@sub 2@ radical density was a decreasing function of the electron density. The H atom density was higher than the CF@sub 2@ radical density in plasmas with electron densities higher than 10@super 12@ cm@super -3@. The spatial distribution of the H atom density in low-density plasmas was roughly uniform, while in high-density plasmas, slightly hollow distributions (i.e., the H atom density in the plasma column was lower than that in the outside region) were observed in the H atom density. @FootnoteText@ @footnote 1@K. Sasaki, M. Nakamoto, and K. Kadota, Rev. Sci. Instrum., in press.

10:20am **PS1-TuM7 c-C@sub 4@F@sub 8@/Ar Inductively Coupled Plasma Characterization***,* ***M.T. Radtke****, J.W. Coburn, D.B. Graves,* University of California, Berkeley

A study of the composition and structure of a c-C@sub 4@F@sub 8@/argon inductively coupled plasma is reported. In this study, we first measured discharge properties (plasma density, potential and electron energy distribution function) in a pure Ar discharge using a Langmuir probe. In subsequent experiments, small amounts of c-C@sub 4@F@sub 8@ were added to argon and the ion and neutral plasma composition was measured using separate quadrupole mass spectrometers. Neutral species number densities were measured using a calibrated, molecular beam sampled, appearance potential mass spectrometer. The dominant radicals were CF@sub 2@ and CF@sub 3@. Positive ions were measured in a separate mass spectrometer. The dominant positive ions were Ar@super +@, CF@super +@, CF@sub 2@@super +@, CF@sub 3@@super +@, C@sub 2@F@sub 4@@super +@, and C@sub 3@F@sub 5@@super +@. The neutral gas temperature was estimated using optical emission spectroscopy of the rotational temperature of trace N@sub 2@ in an argon discharge. Using the measurements, the total dissociation rate coefficients for c-C@sub 4@F@sub 8@ were estimated with a volume-averaged balance on c-C@sub 4@F@sub 8@ for each of the experimental conditions. From the measured EEDFs and the total dissociation rate coefficients, we tested a proposed total dissociation cross section. The proposed cross section was found to be consistent with the measured values to within the experimental uncertainty.

10:40am **PS1-TuM8 Use and Limitations of In-situ FTIR Spectroscopy for Fluorocarbon Plasma Analysis***,* ***B.A. Cruden****, M.V.V.S. Rao,* Eloret Corp., NASA Ames Research Center*; S.P. Sharma, M. Meyyappan,* NASA Ames Research Center

Fourier Transform Infrared (FTIR) Absorption Spectroscopy has been used in an inductively coupled GEC Reference Cell for analysis of CF@sub 4@ plasmas. It was possible to detect undissociated CF@sub 4@ fraction and quartz window etch products (SiF@sub 4@, CO, COF@sub 2@) with this technique. From knowledge of the rotational/vibrational structure of the various bands, it is also possible to extract a gas rotational and vibrational temperature from this data. In interpretation of this data, many of the oft-ignored non-idealities of quanitative FTIR analysis are addressed. Of particular concern is the fact that Doppler-broadened absorption lines are significantly smaller than the instrument resolution. The resulting data represents a non-linear averaging of closely spaced absorbing lines. This produces cross-sections that do not obey Beer's law, i.e. are not constant. By examining the theory behind FTIR, these variations in cross-section are predicted for CF4. These theoretical errors are also manifested in inaccuracies in analyzing overlapping spectra. In FTIR, (as well as other absorption techniques) there is an additional averaging of absorption spectra over spatial coordinates. As a significant portion of the absorption signal will typically lie outside of the plasma, this averaging results in measurements that are not representative of the plasma species in terms of both number density and temperatures. When combined with the resolution limitations, it is predicted that a maximum measurable temperature exists that can differ significantly from the true plasma temperature. The results of a more carefully controlled absorption pathlength will also be presented.

11:00am **PS1-TuM9 Measurements and Models of Ion Energy Distributions in High-Density, Radio-Frequency-Biased CF@sub 4@/Ar Discharges***,* ***M.A. Sobolewski****, Y. Wang, A.N. Goyette,* National Institute of Standards and Technology

Ion dynamics in the narrow sheaths of high-density plasmas, especially in sheaths biased by radio-frequency (rf) voltages, are complicated and nonlinear. Models of such high-density, rf sheaths are needed to predict ion bombardment energies in simulations of high-density plasma etching. To provide data to test these models, we have measured ion energy distributions (IEDs) in CF@sub 4@/argon discharges in a high-density, inductively coupled plasma reactor, using a mass spectrometer equipped with an ion energy analyzer. Energy distributions of CF@super +@, CF@sub 2@@super +@, CF@sub 3@@super +@, and Ar@super +@ ions were measured as a function of pressure, mixture, inductive source power, rf bias frequency and rf bias amplitude. Simultaneous measurements by a capacitive probe and a Faraday cup provide enough information to completely determine the input parameters of sheath models and allow direct comparison of calculated and measured IEDs. For conditions where the rf bias period is much smaller than, or much larger than, the time it takes ions to cross the sheath, very simple models are able to predict the features of the measured IEDs. When the rf bias period approaches the ion transit time, however, more complicated models are required. One recently developed model@footnote 1@ which include a complete treatment of the time-dependent ion dynamics in the sheath, was found to accurately predict the behavior of measured IEDs over the entire range of rf bias frequency. @FootnoteText@ @footnote 1@M. A. Sobolewski, Phys. Rev. E 62, 8540 (2000).

11:20am **PS1-TuM10 Submillimeter Absorption Spectroscopy of an Inductively Coupled Plasma***, **E.C. Benck**, G. Golubiatnikov, G. Fraser,* National Institute of Standards and Technology

Millimeter and submillimeter (100 GHz to 1 THz) absorption spectroscopy is being developed as a sensor for measuring radical densities and temperatures in processing plasmas for microelectronics. Most molecules, radicals, and ions have transitions suitable for detection with submillimeter waves and the necessary spectroscopic data is available in the literature for determining the absolute radical densities. In addition, the narrow linewidths of cw submillimeter sources are suitable for measuring rotational, vibrational and translational temperatures of radicals. Initial measurements are being conducted with a backward wave oscillator (BWO) source and a liquid-He-cooled bolometer detector. Radical densities have been measured in an inductively coupled Gaseous Electronics Conference (GEC) RF Reference Reactor. At frequencies around 100 GHz, large absorption signals can be observed for CHF@sub 3@. Significant amounts of molecular dissociation can be measured when the discharge is ignited. The plasma does not significantly increase the translational temperature, probably due to a large volume of cool gas surrounding the plasma. A 25 times increase in sensitivity would be expected for absorption measurements with frequencies around 500 GHz. Measurements of C@sub x@F@sub y@ and SiF@sub x@ radical densities will also be presented.

Plasma Science
Room 104 - Session PS2-TuM
Emerging Applications of Plasmas

Moderator: G.M.W. Kroesen, Eindhoven University of Technology, The Netherlands

8:20am **PS2-TuM1 Plasma Applications for Layer Transfer Technology***, **N.W. Cheung**,* University of California, Berkeley **INVITED**

Recent progress in bonding and thin-layer splitting enables a new approach to integrate dissimilar thin-film electronic materials. The transfer process incorporates the bonding of two substrates and the use of an ion-cut technique to separate thin films of semiconductors onto various receptor substrates. This paste-and-cut method is an appealing alternative to heterogeneous epitaxial growth approaches because each material layer for a given function can be grown/fabricated on an ideally suited substrate and then combined with a dissimilar receptor substrate. Plasma activated direct bonding and plasma implantation are two key process modules for the success of the layer transfer approach. We will present both low-temperature bonding results using plasma surface activation and ion-cut results using plasma implantation. Material systems such as silicon-on-insulator, III-V semiconductors, and MEMS will be used as examples to illustrate versatility of this approach. Transfer of patterned materials and prefabricated devices have also been proven successful using this technique. * Supported in part by the California SMART Program and National Science Foundation XYZ-on-a-Chip Program.

9:00am **PS2-TuM3 High Density Discharges in Magnetic Fields: Examples of Plasma Thrusters and RF Ion Sources***, **A.B. Bouchoule**, M. Irzyk, M. Prioul,* GREMI Laboratory, Orléans University, France **INVITED**

Magnetized plasmas are involved in various fields of research and applications for their ability to improve power deposition and reduce transport phenomena in gaseous discharges. Two illustrations are described in this contribution. The first one concerns plasma thrusters for space applications, based on the so-called "closed electron drift" discharges. The idea to use Eï,´B situations in order to achieve simultaneously a high ionization efficiency and an acceleration of the produced ions, at a level close to the discharge voltage, was initiated in the sixties.The improvements of these devices, and the present requirements for satellites control in space, lead to active R&D programs devoted to these thrusters. Their proved efficiency is already very high, but insights on their complex physics remains required, in order to improve modeling and simulations able to predict optimized designs. Obtained within the frame of a national program, results on time averaged or transient phenomena occurring in these thrusters will be described. From the experimental point of view, specific electrical and optical diagnostics have been developed and will be reviewed. In connection with modeling studies, these data improved our understanding of physical properties of these thrusters, both for their transient and time averaged behavior. The second one concerns high density ion sources, derived from RF inductive discharges in atomic or molecular gases, and using conventional gridded extraction system. Discharges have been obtained in various magnetic field configurations by using a "Nagoya type" external antenna. Results show the impact of the magnetic topography on efficiency and other characteristics of such ion sources. High atomic ion current densities have been obtained both for oxygen and nitrogen discharges. An extensive PIC simulation code for such high current density sources has been developed and will be presented,with its experimental validation.

9:40am **PS2-TuM5 Characterization of Toroidal Plasma Sources for Semiconductor Processing Applications***, **T. Tanaka**, C. Lai, M. Cox, T. Nowak, S. Wolff, S. Shamouilian, D. Silvetti, H. Hanawa,* Applied Materials Inc.

Toroidal plasma sources have been widely studied for nuclear fusion applications for several decades. The closed topography of the magnetic field provides a superior plasma confinement capability compared to other configurations. This is exemplified by the success of devices such as Tokamak. Over the last few years, there has been growing interest in the toroidal configuration for semiconductor processing applications. Because of the shape of the plasma, the source was primarily considered for downstream remote processing. In this context, plasma confinement is not as important due to the relatively high operating pressures typically used (100mTorr and above). The emphasis rather is placed on the ability to couple the inductive field much more effectively than with a conventional inductively coupled plasma (ICP) source while all but eliminating electrostatic coupling of RF power. Furthermore, by using a magnetic core to couple the driving inductive field, it is possible to operated these source at frequencies less than 400kHz. This is advantageous from the commercial stand point, because of the availability of inexpensive components for the power generator designed to operate at these lower frequencies. At Applied Materials, we have studied electrical properties of toroidal plasma sources. Experimental data is compared to a simple transformer model. We show that power coupling efficiency with these sources is extremely high. Coupling can exceed 98%, which is much higher than with a regular ICP. We also discuss some of the applications of these sources including CVD chamber cleaning

10:00am **PS2-TuM6 Syntheses of Carbon Nanotubes and Nanocapsules by Plasma Chemical Vapor Deposition***, **Y. Hayashi**, M. Kawana, S. Nishino,* Kyoto Institute of Technology, Japan

Carbon nano-materials such as nanotubes, fullerenes, or nanocapsules have been synthesized by the methods of arc discharge, laser evaporation, and thermal chemical-vapor-deposition (CVD). Recently it was reported that multi-wall carbon nanotubes were grown being well aligned perpendicularly to substrates of catalytic metals by plasma CVD, and they are expected to be used for a field emission display. From these results, we came to think that fine-particles of carbon nano-materials can be synthesized by glow-discharge plasma CVD. Fine-particles are suspended in a glow-discharge plasma for a long period because they are negatively charged in it. Therefore larger fine-particles composed of nano-materials can grow in the plasma. And also the modification and control of the materials are expected being suspended in a plasma. A surface-wave-excited 2.45GHz-microwave plasma was used for the syntheses. It was generated in a vacuum chamber by a microwave propagating through a slot antenna. A fine-particle collector, whose electric potential can be controlled from the outside, was put below the plasma. The gas of 10-40 % methane diluted in hydrogen was introduced into the chamber under a gas pressure of 100-700 Pa. Collected fine-particles were analyzed by scanning electron microscopy. Materials of tubular structure of 50-100 nm in diameter and cavity-like spherical and cubic structures of 100-200 nm in size were observed. They should be carbon nanotubes and nanocapsules. Detailed analyses by transmission electron microscopy are going to be performed.

10:40am **PS2-TuM8 The Development of the VASIMR Engine for Space Propulsion***, **J.P. Squire**, F.R. Chang-Diaz,* NASA, Johnson Space Center **INVITED**

The development of advanced propulsion technologies represents a cornerstone in the successful realization of long-term human space travel. Unlike their robotic precursors, human interplanetary spacecraft must be fast, reliable, "power rich," and be capable of reasonable abort options -- essential features for the preservation of human life. The Variable Specific Impulse Magnetoplasma Rocket (VASIMR) is a new approach to plasma propulsion, which addresses these issues and provides an evolutionary path to fusion rockets, but with immediate and exciting non-fusion applications along the way. A NASA-led research effort, involving government, academia and private industry teams in the United States, is exploring the foundations of this concept, and pursuing its rapid development and test. This presentation will cover the basic principles of VASIMR operation, the latest experimental and theoretical results, as well as the most important technological developments and challenges for the future. Light gas (hydrogen, deuterium, helium and mixtures) helicon plasma production and subsequent Ion Cyclotron Resonant Acceleration (ICRA) are key experimental efforts. High density (~ 10@super 19@ m@super -3@) hydrogen, deuterium and helium plasma discharges have been achieved, with nearly 50% of the injected gas being accounted for in the plasma flow. Recent experiments with a strong magnetic choke (~ 1 tesla) downstream of the helicon source have demonstrated high Mach number (> 1) plasma flows. In certian conditions, high energy (> 50 eV) ion tails have been observed from the helicon source alone. Parametric (e.g. power, gas flow, and magnetic field) studies of the helicon source will be presented. ICRA experiments are in progress, so the configuration and most recent results will be discussed. The conceptual application of the VASIMR to fast human Mars missions, as well as plans for near-term flight demonstrations will also be highlighted.

11:40am **PS2-TuM11 Plasma Etching of Cesium Iodide@footnote 1@***, **X. Yang**, J.A. Hopwood,* Northeastern University*; S. Tipnis, V. Nagarkar, V. Gaysinskiy,* Radiation Monitoring Devices, Inc.

Scintillator films that convert an incident x-ray image into visible light play an important role in many imaging applications. Because of its superior light output (59,000 photons/MeV), high density (4.54 g/cc), high effective atomic number (52) and rugged nature, CsI(Tl) is often the material of choice for scintillator films. For adequate detection of 8-70 keV x-rays, 30-200 µm thick CsI films are needed. Spreading of light in the scintillator volume, however, limits the resolution of the resulting images. To address this problem we are micromachining CsI screens to form a finely pixelated structure. When coated with a low refractive index material, each micro-pixel acts as an optical waveguide that minimizes the spread of scintillation light in the screen. The micromachining process uses a high-density inductively coupled plasma to etch CsI samples held by a heated, rf-biased chuck. Fluorine-containing gases such as CF@sub 4@ are found to enhance the etch rate by an order of magnitude compared to Ar@super +@ sputtering alone. Without inert-gas ion bombardment, however, the fluorine-based etch becomes self-limited within a few microns of depth. The formation of a thick passivation layer on the sidewalls of etched features is confirmed by SEM. EDS indicates the passivation layer has a high ratio of Cs to I. Etching exhibits an Arrhenius-type behavior in which the etch rate increases from ~40 nm/min at 40 C to 380 nm/min at 330 C. This temperature dependence corresponds to an activation energy of 0.13 eV. Similar activation energies have been reported for the electronic sputtering of other alkali halides. This suggests that this CsI etch process, similar to alkali halide sputtering, is rate-limited by the thermal migration of ion-induced defects to the CsI surface. Additional results will support a more complete picture of the etching mechanisms. @FootnoteText@ @footnote 1@This work is supported by the NIH contract No. 2R44 CA76758-02.

Semiconductors
Room 124 - Session SC-TuM

Semiconductor Interfaces and Thin Films

Moderator: L.J. Brillson, The Ohio State University

8:20am **SC-TuM1 Nanometer-scale Studies of Possible Dislocation Charging at GaN Interfaces***, **J.P. Pelz**, H.-J. Im, Y. Ding, E.R. Heller,* The Ohio State University*; B. Heying, J.S. Speck,* University of California, Santa Barbara*; W.J. Choyke,* University of Pittsburgh **INVITED**

Threading dislocations (TDs) in III-Nitride films are thought to be electrically active and of major concern for device applications. Several recent studies of GaN and AlGaN/GaN films suggested that TDs might develop significant fixed negative charge (up to 1 e- every c-axis lattice spacing) at or near the TD core. We have quantified possible dislocation charging near metal/GaN interfaces using ultra high vacuum Ballistic Electron Emission Microscopy (BEEM) measurements of identifiable TDs, which were compared with electrostatic modeling of conduction band (CB) bending due to fixed local negative charge. Surprisingly, measurements of TDs in GaN films (grown by molecular beam epitaxy (MBE) under Ga droplet conditions) do not indicate any negative charge at TDs close to the metal-GaN interface, with an estimated upper limit of ~0.25 (e-)/c along the TDs. In contrast, we generally observe a mild decrease in the local CB at TDs as well as at step edges, which may be due to piezoelectric surface charge induced by local stress variations. We will discuss on-going measurements of near-interface dislocation charging of III-Nitride films grown under different conditions (MBE Ga-poor, MOCVD, etc.) to investigate how growth conditions affect local dislocation charging and local transport behavior. Time permitting, we will also discuss on-going measurements of how the Schottky Barrier height on metal/SiC contacts depends on SiC polytype, interface orientation, and deposited metal. This work was supported by the Office of Naval Research.

9:00am **SC-TuM3 Nanometer-scale Studies of Phase Separation in Compound Semiconductor Alloys***, **B. Shin**, A. Lin, K. Lappo, R.S. Goldman,* University of Michigan*; M.C. Hanna, S. Francoeur, A.G. Norman, A. Mascarenhas,* National Renewable Energy Laboratory

Thin films of compound semiconductor alloys can be grown with a wide range of band gap energies and lattice constants, useful for the development of novel electronic and optoelectronic devices. In most of these systems, growth conditions have been reported for which phase separation occurs. Yet, the thermodynamic versus kinetic origin of phase separation, as well as the experimental conditions for determining the presence of phase separation has been the subject of debate for nearly 20 years.@footnote 1,2@ In thin films of compound semiconductor alloys, both the difference in binary bond lengths and the film/substrate misfit are expected to play a significant role in the initiation of alloy phase separation. In this work, we have examined phase separation in the misfit-free InAlAs/InP system using ultra-high vacuum cross-sectional scanning tunneling microscopy (XSTM) and x-ray reciprocal space mapping. For p-doped thin InAlAs layers, XSTM reveals the presence of isotropic non-uniformities which consist of nanometer-sized clusters. For thicker, undoped InAlAs layers, longer wavelength quasi-periodic modulations perpendicular to the growth direction are apparent. These lateral modulations are observed in both topographic and conductance XSTM images, suggesting that they are due to a combination of compositional and strain variations. A signature of these modulations is also apparent in x-ray reciprocal space maps. Interestingly, the modulation wavelengths increase with film thickness and are notably lower than those reported for similar films grown at higher temperatures.@footnote 3@ Together, these results suggest that phase separation is a thermally activated kinetic process which may be significantly affected by the presence of impurities such as dopants. @FootnoteText@@footnote 1@G. B. Stringfellow, J. Cryst. Growth 65, 454 (1983). @footnote 2@A. Zunger and S. Mahajan, in Handbook on Semiconductors (North-Holland, Amsterdam, 1994), Vol. 3, p. 1399. @footnote 3@H. K. Cho et al, Mat. Sci. Eng. B 64, 174 (1999).

9:20am **SC-TuM4 Scanning Tunneling Spectroscopy on Adsorbate Induced Two Dimensional Electron Systems on InAs(110)***, **J. Klijn**, M. Morgenstern, Chr. Meyer, D. Haude, R. Wiesendanger,* Hamburg University, Germany

Two dimensional electron systems (2DES) are usually prepared in heterostructures and thus buried below the surface. Scanning probe methods are consequently restricted to resolutions above 100 nm.@footnote 1@ To increase the spatial resolution, we have prepared an adsorbate induced 2DES close to the surface on n-type InAs(110).@footnote 2@ We measured the local density of states of this 2DES in zero and in finite magnetic field (T=6K, B<=6T). The data at zero field reflect the scattered wave functions at the residual dopants. The corresponding Fourier transformation identifies the k-vector of the undisturbed 2DES as the strongest contribution. However, mixing with other k-vectors due to the potential scattering leads to broadening of the k-space features. The magnetic field data show Landau quantization of the 2DES and exhibit distinct changes in the local density of states. @FootnoteText@ @footnote 1@ S.H. Tessmer et al., Nature 392(1998)51; N.B. Zhitenev et al., Nature 404(2000)473; P. Weitz et al., appl.Surf.Sci. 157(2000)349 @footnote 2@ M. Morgenstern et al., Phys. Rev.B 61(2000)13805.

9:40am **SC-TuM5 InAs Surface Passivation for Electronics and Biosensors***, **D.Y. Petrovykh**,* University of Maryland, College Park*; M.J. Yang, L.J. Whitman,* Naval Research Laboratory

Many semiconductor-based chemical and biological sensors operate by detecting changes in the device conductivity caused by adsorption of organic or inorganic molecules on the sensor surface. The conductivity is affected by the surface charge induced by adsorbates, so sensors based on very thin films or nanostructures should be inherently more sensitive. InAs is a natural material for these applications, because the charge accumulation layer, naturally formed on its surface, provides intrinsic conductivity down to nm-scales. To be used in chemical/biological sensors, InAs films and nanostructures must be properly passivated and functionalized. Ammonium sulfide treatment, commonly used in GaAs processing, is known to effectively remove the oxide and other surface contaminants. We show that it also offers sub-5 nm etching, and the resulting S-passivated surface resists oxidation during short-term exposure to ambient air, or immersion in water (with a range of pH) or organic solvents. We will discuss the possibility of using alkanethiol films for longer-term stability and surface functionalization, including the use of selective deposition by dip-pen nanolithography. For sensor applications, it is also important to control the surface Fermi level pinning. We use conductivity measurements and electron spectroscopy to examine band bending in InAs films and the effects on the conductivity of different capping layers, passivation treatments and other common device processing steps. @FootnoteText@ This work was carried out at the Naval Research Laboratory and supported by the Office of Naval Research, National Nanotechnology Initiative Program on the Nanoscience Basis for Miniaturized, Intelligent Sensors.

10:00am **SC-TuM6 Formation of Co Silicides on Si@sub 0.7@Ge@sub 0.3@ Layer in the Presence of Thin Interposing Au Layer and Capping Ti Layer*, W.W. Wu*,** *T.F. Chiang, S.L. Cheng, H.H. Lin, L.J. Chen,* National Tsing Hua University, Taiwan, R.O.C.*; H.H. Cheng, Y.H. Peng,* National Taiwan University, Taiwan, R.O.C.

Strained SiGe alloys offer the possibility of bandgap engineering for silicon-base devices. Due to their high mobility, SiGe/Si heterostructures have been investigated for use as SiGe channels in MOSFET@super '@s as well as high speed and high transconductance MODFET@super '@s, elevated source-drain contacts and gate material in CMOS technologies. Silicide/Si@sub 1-x@Ge@sub x@/Si(001) heterostructures are promising structures for use in devices such as the heterojunction bipolar transistor and infrared detectors with high cutoff wavelength. Due to its low resistivity, low Schottky barrier, good thermal stability, and possibility of self-aligned formation at relatively low temperatures, CoSi@sub 2@ is an attractive contact material for submicron Si devices. However, in the Co/Si@sub 0.7@Ge@sub 0.3@ system, the CoSi@sub 2@ tended to agglomerate at relatively low temperatures. The formation of Co silicides on Si@sub 0.7@Ge@sub 0.3@ alloys with a thin interposing Au layer and capping Ti layer has been investigated. CoSi@sub 2@ was observed to be the only silicide phase in Si@sub 0.7@Ge@sub 0.3@ samples annealed at 650-950 °C with a thin interposing Au layer and capping Ti layer. The sequence of phase formation is the same as the reaction of Co with single-crystal Si. The presence of Au was found to decrease the formation temperature of CoSi@sub 2@ by about 300 °C compared to that of Co(30nm)/Si@sub 0.7@Ge@sub 0.3@ samples. In addition, a thin capping Ti layer improves the uniformity and thermal stability of CoSi@sub 2@ layer. For Ti(5nm)/Co(30nm)/Au(1nm)/Si@sub 0.7@Ge@sub 0.3@ system, the process window of CoSi@sub 2@ was extended to 650-950 °C. SIMS analysis indicated that a large amount of Au diffused from the Co/Si@sub 0.7@Ge@sub 0.3@ interface to disperse in CoSi@sub 2@ layer during annealing.

10:20am **SC-TuM7 Intrinsic Defects of Cl-doped ZnSe Epitaxial Layers Examined by Photothermal Spectroscopy*, K. Yoshino*,** Miyazaki University, Japan*; M. Yoneta, K. Ohimori, H. Saito, M. Ohishi,* Okayama University of Science, Japan

Photothermal (PT) measurements have recently been carried out as one of the new methods to study the physical properties of semiconductors. One of the great advantages of the PT measurements is that the nonradiative carrier recombination processes are measured directly. Therefore, the PT may complement a photoluminescence (PL) and PL excitation (PLE). Furthermore, the PT also is much easier than deep-level transient-capacitance spectroscopy (DLTS) since no electrodes are needed in the PT system. In our previous paper,@footnote 1@ the PT measurements were carried out for nondoped and N-doped ZnSe epitaxial layers grown by molecular beam epitaxy (MBE), and we obtained the nonradiative carrier recombination centers in those samples. In this paper, we carried out the PT and PL measurements on Cl-doped ZnSe epitaxial layers from 80 to 300 K. The net carrier concentration is from 5.8 ´ 10 @super 17@ to 2 ´ 10@super 18 cm@super 3@. Three distinct peaks correspond to bandgap energy of ZnSe and two kinds of Cl related centers are observed. The activation energies of the Cl defects are estimated to be about 25 and 250 meV. The energy of 25 meV is known to be an activation energy of Cl atom in the Se site and the energy of 250 meV is not unknown. The emission due to the deep defect is not observed in the PL spectrum. Therefore, it indicates the defect with an activation energy of 250 meV acts the nonradiative carrier recombination center. @FootnoteText@ @footnote 1@ K. Yoshino et al., J. Crystal Growth 214&215 (2000) 572.

10:40am **SC-TuM8 Metal-Induced States and Polytype Transformations at SiC Interfaces*, S.P. Tumakha,*** *L.J. Brillson, G.H. Jessen,* Ohio State University*; R.S. Okojie, D. Lukco,* NASA-Glenn Research Center

We have used low energy electron-excited nanoluminescence (LEEN) spectroscopy to probe electronic structure at chemically-treated and metallized 4H and 6H-SiC interfaces. SiC high temperature electronics requires metal contacts with controllable barriers and minimal deep level electronic states. LEEN spectra over incident electron beam energies E from 0.5 to 5 keV identify the presence of localized states and their spatial distribution on a nanometer scale. With increasing E, the electron cascade and resultant generation of free electron-hole pairs peak at increasing depth ranging from 10 nm at 0.5 keV to 200 nm at 5 keV. The resultant band-to-band and band-to-defect luminescence is detected selectively at the intimate metal-SiC interface, the near-interface region extending tens of nanometers into the SiC, or the bulk SiC up to 0.2 microns into the solid. Pt/Ti/SiC junctions were prepared by standard cleaning, oxidation, and etching methods. 6H-SiC exhibits optical emission that varies with depth from the intimate interface and with surface chemical preparation. The depth-dependent spectra exhibit 2.9 eV near band edge (NBE) features of 6H-SiC for bulk excitation vs. a disordered and/or defected region within a few nm of the metal contact. Spectra from the near interface region indicate the existence of a SiC polytype with a higher band gap of ca 3.4 eV - resembling 4H-SiC as well as a discrete deep level, i.e., emission energy = 1.9 eV, for a specific surface treatment. Metal-induced features on 4H-SiC are similar. In addition, oxidation before or after metallization produces 2.5 eV emission extending hundreds of nm into the 4H bulk, characteristic of polytype conversion to 3C-SiC and confirmed by TEM. A strong impurity doping dependence suggests that oxidation or metallization-induced strain drives this transformation. The structural as well as electronic changes at SiC interfaces have significant device and processing implications.

11:00am **SC-TuM9 Growth and Electrical Characterization of Ultra-Dense Phosphorous Delta-Doping Layers in Silicon*, T.-C. Shen*,** *J.-Y. Ji,* Utah State University*; M. Zudov, R.-R. Du,* University of Utah*; J.S. Kline, J.R. Tucker,* University of Illinois

If dopant atoms substitute a substantial fraction of a monolayer of the Si atoms within a crystal, the resulting 2D dopant sheet may provide unique electrical properties for novel nano-scale devices. We have demonstrated that depositing phosphine molecules onto Si(100) surfaces in ultrahigh vacuum, followed by 35-50ML of Si epitaxy at T<500K, can yield a conducting layer that does not freeze out even at 0.3K. At 1/4ML saturation coverage at room temperature, the positive phosphorous ions create very large electric fields in the growth direction, producing a tightly confined 2D electron system. Within the plane, however, wavefunctions for these bound electrons are expected to couple across relatively large distances of a few Bohr radii (~2.5nm for P-atom donors), opening up new possibilities for lateral tunnel junctions. Initial magnetotransport measurements reveal an electron density of ~ 2.6x10@super 14@cm@super -2@ (~1/4ML) at 0.3K indicating complete electrical activation of the donor layer. From 60 to 0.3K the sheet resistance grows logarithmically with decreasing T, yielding a resistance of 1.16 k@ohm@/sq and a mobility of 21cm@super 2@/Vs at 0.3K. Studies of the correlation between electrical characteristics and phosphine deposition parameters will be presented. In addition, a new paradigm for devices based on selectively patterned 2D electron/hole systems will be discussed.

Surface Engineering
Room 132 - Session SE-TuM

Surface Engineering II: Cleaning, Modification, and Finishing

Moderator: L.-Q. Wang, Pacific Northwest National Laboratory

8:20am **SE-TuM1 PVD Surface Engineering Utilising Combined Steered Cathodic Arc and Unbalanced Magnetron Sputter Deposition,** **INVITED**

The application of combined steered cathodic arc evaporation and unbalanced magnetron sputtering utilising closed magnetic field conditions generated by electromagnets raises a broad field of opportunities to surface engineering of metallic substrate materials. Low pressure plasma nitriding (5.10@super -1@ Pa) as well as low energy metal ion implantation (U@sub s@-1200 V) with steered arc discharge as ion source allow the synthesis of substrate/ coating interfaces specifically tailored to the demands of the actual application. Nitriding as deep as 20µm and Cr ion implantation to a depth of 20nm create a surface chemistry, which enhances the adhesion and encourages localised epitaxial growth of the reactively magnetron sputter deposited nitride films. Alternatively semi-implanted micro-crystalline Nb deposits may be formed, which represent an excellent pre-treatment for corrosion and wear resistant hard coatings. Due to the outstanding adhesion and the graded film architecture, including a stress gradient inducing base layer, superhard- superlattice coatings with a period of approximately 3.5 nm based on TiAlN (TiAlN/CrN, TiAlN/VN, TiAlN/ZrN) and CrN (CrN/NbN) showing Hp values > 40 GPa have been produced exhibiting comparable coating productivity to monolithically grown nitrides like TiAlN and CrN. Despite residual stresses in the coatings up to -7 GPa critical load values L@sub c@ > 50N and HRC indentation class "1" were achieved. Finally, TiAlN coatings with layered Y incorporation have been especially designed for dry high speed cutting of HRC>60 die steel and coating of hot forging tools for working temperatures >900°C.

9:00am **SE-TuM3 Surface Processing of Large-scale FEL SS Test Electrodes by PSII/PVD to Suppress Field Emission***, **L. Wu**, D.M. Manos,* College of William and Mary*; F. Dylla, C. Sinclair, T. Siggins,* Thomas Jefferson National Accelerator Facility

Large-scale highly polished stainless steel test electrodes for FEL electron injection gun have been processed by an integrated PSII/PVD system to suppress field emission. Hand polishing, which is very time-consuming and difficult, has been the main technique used to reduce field emission from these large 3-D electrode structures. Even after extensive polishing, the performance of the electrodes has been found to be unpredictable, with turn-on voltages varying by factors of 2 or more for similarly prepared electrodes. Prior to this work, the maximum practical operating field gradient was 3-6 MV/m, with a dark current of several nA. With a 0.61 m I.D. chamber, 0.57 m I.D. quartz window, and 0.43 m I. D. RF antenna, the PSII/PVD system used in this study is capable of large-area plasma source ion implantation and also of PVD of high purity SiO2 films over stainless steel, with adjustable nitrogen concentrations. Both the PSII and PVD processes are performed at low substrate temperatures, critical to keeping the original electrode surface profile and surface finish. Two recipes were developed, using DC glow discharge cleaning prior to HV pulse implanting to condition the electrode surface and to prevent arcing during implantation. In addition to the test electrodes, witness samples processed under similar conditions were studied by AES depth profiling, SIMS, variable angle spectroscopic ellipsometry, and micro-hardness testing. Results will be reported in detail. Field emission tests of the processed large-area electrodes showed that the electrodes were able to quickly achieve a field of 30 MV/m after minimal conditioning, and to hold this field for long periods with a dark current of only 160 pA. The implications for accelerator structures will be described.

9:20am **SE-TuM4 Noncontact Physical Removal of Nano-scale Particles from Surfaces***, **A.A. Busnaina**,* Northeastern University*; H. Lin,* Clarkson University

There is a need to physically manipulate, control or remove nanoscale particles. The removal of nanoscale particles physically without substrate damage or alteration is needed in nanoscale manufacturing. It is needed to remove existing contaminants from a substrate. Even in the semiconductor industry, such a need is a projected requirement in 2011. However, this need is required toady in nanoscale fabrication. Physical non contact removal using high frequency acoustic streaming had been used to remove submicron particles. However, the removal of 100 nm particles and smaller is becoming a serious challenge. Busnaina et al.@footnote 1@ studied megahertz streaming particle removal and evaluated the effect of acoustic streaming on the cleaning process. High frequency acoustic streaming is a promising technique for nano-scale particles removal. Using DI water, the removal of nano-size particles down to 10 nm can be best accomplished using acoustic streaming with frequency above 1.3 MHz. As the frequency increases, the acoustic boundary layer thickness decreases and the streaming velocity increases thereby increasing the drag force and consequently the removal moment. Softer particles (such as PSL) are more difficult to remove than hard particles (such as silica), because of adhesion-induced deformation, needing a much higher frequency. The experimental results show that a complete removal of silica particles down to 100 nm is achievable. . @FootnoteText@ @footnote 1@Busnaina, A. A. and Gale, G. W, Journal of Particulate Science and Technology, 17(3), 1999.

9:40am **SE-TuM5 Photoresist Removing using Atomic Hydrogen Generated by Heated Catalyzer***, **A. Izumi**, H. Matsumura,* Japan Advanced Institute of Science and Technology (JAIST), Japan

It is well known that photoresist films play an important role to define very small pattern, selective etching, ion-implantation process, etc. The residues of photoresist films after these processes should be completely removed. Wet cleaning using a sulfuric acid and a hydrogen peroxide mixture succeeding to O@sub 2@ plasma ashing is used as a conventional removing method of the residues. However, this conventional method is not effective for removing high doped ion-implanted resists. O@sub 2@ ashing plasma induces a lot of problems such as plasma damage to devices and oxidizes semiconductor substrates and/or interlevel dielectric films. In this work, we propose a novel photoresist removing which is using atomic hydrogen. Atomic hydrogen is generated by decomposition of H@sub 2@ on a heated (1700°C) tungsten catalyzer. Therefore, the plasma damage and the oxidation are not matters of concern. Atomic hydrogen was irradiated to the photoresist coated Si(100) which was doped with B (50 kV, 10@super 15@ atoms/cm@super 2@) by ion-implantation. Following results are obtained. 1) X-ray photoelectron spectroscopy measurements reveal that 1 µm-thick photoresist is removed completely by 15 minutes irradiation of atomic hydrogen. 2) The photoresist removing rates increase as hydrogen flow rate increases. 3) The substrate holder temperature around 85 °C shows the highest photoresist removing rate. 4) Quadruple mass spectroscopy measurements detect a lot of kind of hydrocarbon species during the irradiation of atomic hydrogen. The above results show that this technique is effective for photoresist removing for various kinds of photolithography process.

10:00am **SE-TuM6 Low Temperature Remote Plasma Cleaning of the Fluorocarbon and Polymerized Residues formed during Contact Hole Dry Etching***, **H. Seo**, H. Soh, Y. Kim, Y.C. Kim, H. Jeon,* Hanyang University, Korea

Reducing contact hole resistance in ultra large scale integration becomes very important as the contact hole size getting small.@footnote 1@ Reactive ion etching (RIE) using fluorocarbon is widely used to open contact holes due to its high anisotropic and selective silicon etching characteristics. However, the RIE process induces fluorocarbon residues and results in high contact resistance and defects at the metal-silicon interface. Furthermore, these residues polymerized after photo resist (PR) ashing process. These polymerized residues were reported to be non-volatile, and chemically and thermally stable.@footnote 2@ Therefore, these polymer residues must be removed prior to metal contact. In this study, we investigated the low temperature oxygen and hydrogen remote plasma cleaning of the polymer residues formed at the contact hole during RIE and PR ashing processes. Samples having shallow trench isolation structure were prepared by RIE using CHF@sub 3@/CF@sub 4@ gas. The efficiency of cleaning was systematically evaluated at various conditions such as plasma power, exposure time, gas flow rate and sample temperature. Polymer residues before and after cleaning were analyzed using in-situ Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and atomic force microscope (AFM) systems. Also, the polymer residues were directly observed before and after cleaning using scanning electron microscope (SEM). Carbon and fluorine impurities were significantly reduced below detection limit of AES after remote plasma cleaning. Also, the C-C/C-H and C-F@sub x@ (x=1,2,3) types bonding were not observed by XPS. This paper presents the efficiency of the remote plasma cleaning of the polymerized residues formed during RIE and ashing processes at the contact hole. @FootnoteText@ @footnote 1@K. Sakuma, K. Machida, K. Kamoshida, Y. Sato, K. Imai and E. Arai, J. Vac. Sci. Technol. B 13(3), May/June (1995) @footnote 2@J. Fonash, J. Electrochem. Soc. 137, 3885 (1990)

10:20am **SE-TuM7 Polymer Metallization - Comparing the Effect of Pre- and Post Surface Modification on the Cu/PVC and Cu/PTFE Systems***, **C.C. Perry**, S.R. Carlo,* The Johns Hopkins University*; J. Torres,* The Johns Hopkins University, US*; D.H. Fairbrother,* The Johns Hopkins University

The increasing requirements of fabricated industrial materials have provided the motivation for research in metallized plastics. Pre- and post surface polymer modification treatments are usually employed in industrial processes to improve adhesion at the metal/polymer interface. One factor that is believed to be important in improving metal/polymer adhesion characteristics during surface modification is the formation of metal salts at the metal/polymer interface. We present results on the effect of Ar@super +@ ion and X-ray pre- and post treatment strategies on the Cu/PVC and Cu/PTFE systems with respect to the formation of copper halides. On unmodified PVC, copper reacts to form copper(I) chloride but is unreactive on native PTFE. Post X-ray treatment of metallized PVC and PTFE was found to increase the metal chloride/fluoride content within the metal organic interface due to the production of reactive halogen species (e.g. fluorine radicals). In contrast to Cu/PVC, where copper(I) chloride is formed on both modified and unmodified PVC, the formation of copper (II) fluoride at the Cu/PTFE interface is shown to occur only after post-surface modification by x-rays and Ar@super +@ ions. The extent of copper (II) fluoride production was similar for both Ar@super +@ and X-ray irradiation post-treatment strategies for comparable initial copper coverages, suggesting a common reaction mechanism for the formation of copper (II) fluoride. Results will also be presented showing the effect of co-evaporated titanium on the nature of the Cu/PTFE interface.

10:40am **SE-TuM8 Metallization of PVC - Physical Vapor Deposition and Effect of Ar@super +@/X-ray Pre and Post Treatment***, S.R. Carlo, C.C. Perry,* The Johns Hopkins University*; J. Torres,* The Johns Hopkins University, US*; D.H. Fairbrother,* The Johns Hopkins University

Metallization of polymers is important commercially in both the microelectronic and conventional industries, having applications in the processing of thin film-transistors, compact discs and decorative overlayers. The nature of the metal/polymer interface is especially important with respect to adhesion of the polymer to the overlayer and in semiconductor electrode-polymer connections where diffusion of metal from the polymer into the dielectric can cause capacitance problems. Understanding the process of metallization will enable such problems to be addressed. In this study, we present results on the evolution of the metal-poly(vinylchloride) (metal/PVC) interface using X-ray photoelectron spectroscopy (XPS) following physical vapor deposition of Fe, Ti, Ni, Cu and Au. All of the metals reacted, forming a metal chloride with subsequent deposition of a metallic overlayer. The extent of reaction (as measured by the relative amount of metal chloride production) increased in the order Ti > Fe > Cu > Ni > Au. In all cases, the metal chloride was in the lowest oxidation state e.g. FeCl@sub 2@ and AuCl. The effect of sample pre and post-treatment was also investigated. Pre-treatment of PVC by Ar@super +@ ions increased the yield of FeCl@sub 2@ compared to unmodified PVC. There was negligible difference in the Cu/PVC system, while in the Au/PVC system, the yield of metal chloride was lower compared to unmodified PVC. Post-metallization X-ray treatment increased the metal chloride concentration for each metal/PVC system.

11:00am **SE-TuM9 Does Thermal Spike Effect Ion Mixing at Ion Energy Lower than 1.5 keV?***, **M. Menyhard**, G. Zsolt,* Research Institute for Technical Physics and Materials Science, Hungary*; P.J. Chen, C.J. Powell, L. Gal, W.F. Egelhoff,* National Institute of Standards and Technology

Experimentally measured (Auger, XPS) depth profiles cannot be properly evaluated without knowing the ion sputtering induced alteration. The presently used evaluation routines assume that ballistic mixing occur. It was suggested and some experimental evidences have been presented, however, long time ago, that the thermal spikes might be operating even at low ion energies causing enhanced mixing. Systematic studies on the appearance of thermal spikes in case of depth profiling applying low energy (less than 1.5 keV) ions sputtering has been carried out. Periodic double-layer structures (consisting 10 layer pairs) with double-layer thickness of 4 nm were grown by sputter deposition from pair of elements exhibiting high (Pt-Ti) and low solubility (Pt-Co, Ni-Ti, Co-Ti). Auger spectroscopic depth profiling was carried out with parameters of: specimen rotation, grazing angle of incidence, argon ions, energy range 0.3-1.5 keV. The ion mixing in these periodic structures can be measured by the amplitude of oscillation of the depth profile. The amplitude of oscillations in all cases was linearly dependent on the square roote of ion energy. Thus in the energy range studied a single mechanism was responsible for the ion mixing. Since we cannot suppose that at the 0.3 keV irradiation thermal spikes form it seems that the ion mixing in these cases are governed by ballistic mixing. The depth profiles were also simulated by T-DY4 code assuming ballistic mixing. The difference of the simulated and measured depth profiles was explained by interface roughness.

Surface Science
Room 120 - Session SS+BI-TuM

Poirier Memorial Session: Self-Assembled Monolayers I

Moderator: N.D. Shinn, Sandia National Laboratories

8:20am **SS+BI-TuM1 Greg Poirier's STM Landscapes of Alkanethiol Monolayers on Gold: A Retrospective***, **M.J. Tarlov**,* National Institute of Standards and Technology **INVITED**

The surface science community lost one of its bright young stars, Gregory E. Poirier, who passed away in September at the age of 39. During Greg's brief career at NIST he made many noteworthy contributions in the areas of surface science and chemical sensing, however, it was his STM studies of alkanethiol self-assembled monolayers (SAMs) on gold that earned him the greatest recognition. Greg's STM images were some of the first to reveal the structural complexity and phase behavior that governs the 2-D world of alkanethiols on gold. Through meticulous and rigorous interpretation of these images he unlocked many structural details of SAMs and gained an understanding of the molecular forces that govern the assembly of SAMs. This talk will review some of the highlights of Greg's STM studies including the rich variety of molecular-scale crystal structures of alkanethiol SAMs, their associated defect structures, and the development of a general mechanism for SAM formation.

9:00am **SS+BI-TuM3 Imaging and Diffraction: Two Complementary Probes of Self-Assembled Monolayer Structure and Properties***, **G. Scoles**,* Princeton University **INVITED**

Using Self-Assembled Monolayers (SAMs) as test systems, a few introductory examples of the well known complementarity between imaging (local SAM structure and defects) and diffraction (precise determination of overall SAM structure) will be given. Starting from the pioneering detection, by Poirier, of the c(4x2) superlattice superimposed to the basic hexagonal structure of alkylthiol SAMs on Au(111), we will review the present status of the question concerning the presence of at least two inequivalent sulfur atoms in the equilibrated monolayers. After reviewing the overwhelming experimental evidence that points in that direction, we will present recent Density Functional Theory calculations that may finally provide a way out of this ten year old controversy. Returning to the complementarity between imaging and diffraction, we will point out a few less known features of both methods. In particular, the sensitivity of atomic beam diffraction to very small vertical displacements (not detectable with either X-rays or STM) will be discussed along with the possibility, offered by X-rays, to provide information on buried SAM interfaces. We will conclude showing how the synthetic flexibility afforded by SAMs coupled with the local sensitivity of STM provides unique opportunities to understand electron transfer processes at the organic/metal interface.

9:40am **SS+BI-TuM5 Characterization of Self-assembled Monolayers Using Near-edge X-ray Absorption Spectroscopy***, **T.M. Willey**,* Univ. of California at Davis and Lawrence Livermore National Lab*; A.L. Vance, A.W. vanBuuren,* Lawrence Livermore National Lab*; C.F.O. Bostedt,* Univ. of Hamburg, Germany, and Lawrence Livermore National Lab*; G.A. Fox, A.J. Nelson, L.J. Terminello,* Lawrence Livermore National Lab*; C.S. Fadley,* Unive. of California at Davis and Lawrence Berkeley National Lab

We have investigated methyl and carboxyl terminated alkanethiols (hexadecanethiol and mercaptohexadecanoic acid) and other more complex self-assembled monolayers (SAMs) on Au(111). We characterize these SAMs using x-ray absorption at the Carbon K-edge, Sulfur L-edge, ans well as Oxygen and Nitrogen K-edges where applicable. Near-edge X-ray Absorption Spectroscopy (NEXAFS) gives information about chemical state, and polarization effects in these spectra probe the orientation of chemical bonds. Simple, carboxyl-terminated alkanethiols supposedly do not form well-ordered films. We currently investigate attachment, uniformity, and order of these films as a function of solvent, chemical state of the carboxyl group, and by intermixing with well-ordering methyl-terminated alkanethiols. We have also investigated attachment and order of more complex, disulfide containing thioctic acid derivatives. Preliminary results indicate that we have been successful in chemisorbing both sulfur-functionalized ends of a number of these molecules to the gold surface. T. Willey acknowledges a Student-Employee Graduate Research Fellowship through LLNL. This work is supported by the U.S. Department of Energy, BES Materials Sciences under contract W-7405-ENG-48, LLNL.

10:00am **SS+BI-TuM6 Structure of Alkyl Thiol and Dialkyl Disulfide on Au(111)***, **H. Nozoye,*** Nanotechnology Research Institute, AIST, Japan*; T Hayashi, C. Kodama,* University of Tsukuba, Japan*; Y. Morikawa,* JRCAT, AIST, Japan

The structure and formation process of self-assembled monolayers on Au(111) have been a long-standing unsolved problem. We determined the adsorption state of alkane thiol and dialkyl disulfide with different alkyl chain length on Au(111), which are prototypical self-assembled monolayer systems, by using temperature programmed desorption (TPD), high sensitivity low energy electron diffraction (LEED), high resolution electron energy loss spectroscopy (HREELS) and density functional theory (DFT) calculation. We concluded that the SH bond of alkane thiol and the SS bond of dialkyl disulfide break below room temperature, spontaneously desorbing hydrogen and resulting in the formation of highly ordered adsorption state of thiolate on the surface. The spectra above 500cm@super-1@ contain the information of the orientation of the alkyl moiety, however, those of low energy region contain the information of the bonding between S and Au. HREELS spectra of low energy region were almost the same for all the thiolate species, irrespective of the difference of the coverage of the thiolate and of the chain length of alkyl moiety, although the spectra above 500cm@super-1@ were changed depending on the coverage of the thiolate species. The change of the HREELS spectra above 500cm@super-1@ agreed with the conclusion obtained from STM measurements, that is the lying-down configuration in the low coverage region and standing-up configuration at the saturation coverage. The HREELS spectra of the low energy region were analyzed with the DFT calculation; The location of S of the thiolate on Au(111) is the bridge site and the SC bond is inclined about 50 degree from the surface normal. From these results we concluded that the structure of the root part of the thiolate species is common, at least for alkyl thiolate with relatively short chain, notwithstanding the difference of the orientation of the alkyl moiety, that is the lying-down and standing-up structures.

10:20am **SS+BI-TuM7 Two-dimensional Phase Diagram of Decanethiol on Au (111)***, **J.M. White,** W.P. Fitts,* The University of Texas at Austin **INVITED**

Based on variable temperature ultrahigh vacuum scanning tunneling microscopy data, we propose a two-dimensional phase diagram of monolayer decanethiol on Au(111). Four triple point temperatures were determined: T@sub1@ at ~ 27 @degree@C, T@sub 2@ at ~ 33 @degree@C, T@sub3@ at ~ 35 @degree@C and T@sub 4@ ~ 56@degree C. T@sub 1@ defines the lowest temperature melting point and T@sub 4@ defines the temperature above which striped phases are metastable. These data provide a fundamental framework to understand and control meso-scale monolayer structure; moreover, they provide fundamental insight into two dimensional phase behavior of molecules with many degrees-of-freedom.

11:00am **SS+BI-TuM9 Odd-Even Effects in the Electron-induced Damage of Biphenyl-substituted Alkanethiol Self-assembled Monolayers***, **M. Zharnikov,** S. Frey, H.-T. Rong,* Universität Heidelberg, Germany*; M. Buck,* University of St Andrews, U.K., Scotland*; K. Heister, M. Grunze,* Universität Heidelberg, Germany

Self-assembled monolayers (SAMs) formed on Au(111) from biphenyl-substituted alkanethiols CH@sub 3@(C@sub 6@H@sub 4@)@sub2@(CH@sub 2@)@sub n@SH (BPn) exhibit odd-even changes in the packing density and the tilt angle of the biphenyl moieties with varying length of the aliphatic part. We have applied X-ray photoelectron spectroscopy, near-edge X-ray absorption fine structure spectroscopy, infrared absorption spectroscopy, and advancing contact angle measurements to study electron beam induced damage in these systems as well as in pure aromatic biphenylthiol (BP0) SAMs on Au substrates. Although the character of the electron-induced damage in all investigated SAMs was found to be similar, the extent and rate of the observed changes exhibited a clear correlation with the packing density and orientation of the biphenyl moieties in the BPn SAMs: The densely packed BPn films are noticeably more insensitive (in terms of the orientational order, irradiation-induced desorption, and anchoring to the substrate) towards electron irradiation than the loosely packed BPn layers. The extent of the irradiation-induced damage in pure aromatic BP0 SAMs was observed to be very close to that in the loosely packed BPn films, which indicates that the former films are in some sense also "loosely packed". Considering the potential applications of the aromatic SAMs as lithographic resist or template, the introduction of the short aliphatic chain in the respective molecules provides a simple and efficient way to manipulate their reaction toward ionizing irradiation in a desirable way. This work has been supported by the German BMBF (05 SF8VHA 1).

11:20am **SS+BI-TuM10 Highly Ordered Organic Monolayers with Reduced Antiphase Domain Walls Due to Growth from Two-dimensional Gas- and Fluid- Phases***, **L. Gross,** C. Seidel, H. Fuchs,* University of Münster, Germany

The growth process of monolayers of perylene and coronene on the metal surfaces Ag(110), Au(110) 1x2 and Au(111) 23x@sr@3 was investigated by means of low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). The preparation was done by molecular beam epitaxy (MBE), with the possibility of LEED or STM measurements during evaporation. Both molecules show (restricted on Au(110) 1x2) an evolution from isotropic disordered structures in the submonolayer regime to a highly (substrate-dependent) ordered monolayer. In all presented systems the adsobate begins to form highly ordered structures just before the coverage of a complete monolayer is reached. The final monolayer structures are coincident, except coronene on Au(111) which is commensurate, furthermore perylene on Au(110) and coronene on Au(111) show uniform domain orientation. The lateral ordering process of these molecules allows epitaxial growth with a reduced density of antiphase domain boundaries, because crystallization does not start from islands in the submonolayer regime, but from two-dimensional gas- and fluid- phases.

Surface Science

Room 121 - Session SS1-TuM

Adsorption on Oxide Surfaces

Moderator: J.A. Rodriguez, Brookhaven National Laboratory

8:20am **SS1-TuM1 Microstructure of the Al@sub 2@O@sub 3@(11-20) Surface and Ultrathin Nb Films***, **G. Witte,** Th. Becker, A. Birkner, Ch. Woöll,* Ruhr-Universität Bochum, Germany

Despite the technological importance of sapphire such as a support for devices or catalysts the microstructure of its surfaces have yet not been investigated in great detail. Here we report on a combined AFM, LEED, HAS and XPS study of the microstructure of the Al@sub 2@O@sub 3@(11-20) surface and the initial growth of ultrathin (110) oriented Nb-films. The samples were first heated in air which leads to atomically flat but carbon coated surfaces as indicated by the AFM and XPS measurements and requires a further preparation by sputtering and annealing to produce clean and well ordered surfaces. The resulting surface structure was found to depend sensitively on the annealing temperature. Heating above 1300K causes a substantial oxygen reduction at the surface which is accompanied by a long ranging highly periodic surface reconstruction without facetting. The subsequent growth of ultrathin Nb-films reveals the well known epitaxial relation between Nb and sapphire but also indicates that the films are not continuos. Instead flat islands are formed in a growth mode similar to that obtained for Ni on diamond.@footnote 1@ @FootnoteText@ @footnote 1@J.Braun, J.P.Toennies and Ch.Wöll, Phys. Rev. B60, 11707 (1999).

8:40am **SS1-TuM2 Growth and Structure of Ultrathin Silver and Silver Oxide Films on Sapphire Surfaces***, F.X. Bock,* University of Maine*; S.B. Rivers,* Rhode Island College*; **R.J. Lad,*** University of Maine

Silver oxide is a p-type semiconductor that has potential applications as a sensing film or optical recording element. Silver is relatively inert towards oxygen and silver oxide is rather unstable. We studied the interactions of Ag with r-cut sapphire (@alpha@-Al@sub 2@O@sub 3@) surfaces at ambient temperature resulting from (i) thermal evaporation of Ag in UHV, (ii) evaporation of Ag in molecular O@sub 2@, and (iii) evaporation of Ag in the presence of an electron cyclotron resonance (ECR) oxygen plasma source. Pure Ag deposited in UHV grows with a random polycrystalline structure. However, when Ag is evaporated in a 10@super -4@ Torr molecular O@sub 2@ background, epitaxial Ag growth with (110) orientation is observed as determined by RHEED and XRD. No oxygen is incorporated in the film as measured by XPS and only a slight lattice mismatch at the Ag/sapphire interface is found suggesting that the adsorbed oxygen acts as a surfactant in influencing the Ag nucleation and surface transport. Using an ECR oxygen plasma, Ag@sub 2@O is formed with a structure being dependent on deposition rate; below 0.2 Å/s, (111) orientation is formed while at faster rates the oxide is amorphous. The Ag@sub 2@O films are unstable above ~180@super o@C. AFM observations of the evaporation process following vacuum annealing treatments indicate that the decomposition occurs through a nucleation process leaving behind metallic Ag clusters on the bare sapphire.

9:00am **SS1-TuM3 STM Study of Metal Growth on ZnO Surfaces**, ***O. Dulub,*** Tulane University; *L.A. Boatner,* Oak Ridge National Laboratory; *U. Diebold,* Tulane University

Metals on ZnO surfaces are widely applied in catalysis, gas sensing, and microelectronic fabrication. The morphology of the polar zinc-terminated (0001) and oxygen-terminated (000-1), as well as the non-polar (10-10) and (11-20) prism faces of ZnO was investigated with STM. Images of polar surfaces, prepared by sputtering and annealing at 500-750°C, show two types of terraces rotated by 60° with respect to each other. Mono-atomic steps alternate between straight and saw-toothed profiles. Increasing the annealing temperature to 800°C smoothes the surfaces but creates a higher density of small holes on the stepped terraces. A (1x3) reconstruction was observed on the ZnO (000-1) surface after annealing at 750°C. After sputtering and annealing the ZnO (10-10) surface at 550â€“700°C, the terraces are separated by steps running along either [000-1] (type A) or [11-20] (type B) directions. The same treatment of the ZnO (11-20) surface leads to a â€œwavyâ€� surface morphology, i.e., hills (consisting of small terraces) with an average height of 80Å and a separation of 55Å. Near-atomic resolution was achieved on both non-polar faces. Cu nucleation is strongly correlated with surface defects. Cu deposited on a "freshly-annealed" ZnO (10-10) surface shows preferential nucleation of exclusively 3D islands oriented perpendicular to the atomic row direction at the step edges. When the density of impurity atoms on the terraces is high, both 2D and 3D islands are randomly distributed across the terraces. These results are compared with those obtained for growth of Cu and Pt on the other faces of ZnO. Work performed at Tulane was supported by a NSF-CAREER grant. ORNL is supported by the U.S. DOE-BES under contract No. DE-AC05-96OR22464.

9:20am **SS1-TuM4 Metal - Support Interactions between Pt and Thin Film Cerium Oxide@footnote 1@**, ***D.R. Mullins***, *K. Zhang,* Oak Ridge National Laboratory

We have examined the interaction between Pt and reduced or oxidized cerium oxide (CeO@sub X@). Reduced CeO@sub X@ strongly modifies the chemisorption of CO on the supported Pt. Two different modifications are evident depending on how the sample is annealed. If the sample is annealed to greater than 800 K, the amount of CO that adsorbs on the Pt at 150 K is dramatically reduced. In addition, annealing at elevated temperatures decreases the Pt XPS intensity significantly. These results suggest that, similar to Pt on reduced TiO@sub X@, the Pt is covered by the reduced CeO@sub X@ at elevated temperatures. If the sample is annealed to 700 K or less before CO is adsorbed at 150 K, there is no decrease in the amount of CO that adsorbs. However, the CO desorption temperature is shifted to a much lower temperature compared to CO adsorbed on a Pt single crystal. This shift in the CO desorption temperature is ascribed to a weakening of the CO - Pt bond that results from an electronic interaction between the Pt and the reduced ceria. The behavior of Pt on CeO@sub X@ is very different from Rh on CeO@sub X@. The CO - Rh bond is strengthened on CeO@sub X@ compared to Rh single crystals and there is an increase in the CO dissociation activity. Rh also shows no evidence of encapsulation when annealed to higher temperatures. CO desorption from Pt on oxidized CeO@sub 2@ resembles that observed from Pt on Al@sub 2@O@sub 3@ and from Pt single crystals and therefore indicates no significant modifications of the Pt chemisorption properties by the CeO@sub 2@. @FootnoteText@ @footnote 1@Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

9:40am **SS1-TuM5 Electronic Structure of Epitaxial Thin NiO(100) Films Grown on Ag(100): Towards a Firm Experimental Basis**, *L. Duò, M. Portalupi, G. Isella, R. Bertacco,* ***M. Marcon***, *F. Ciccacci,* Politecnico di Milano, Italy

In the field of electron correlations in solids NiO definitely plays a key role. A large amount of work on the electronic and magnetic properties of NiO has been done, but the longstanding problem of the full description and understanding of its electron states is still open. While for photoemission (PE) results on NiO a large set of data is available in literature, with a general consensus on the lineshapes, concerning inverse PE (IPE) only few pioneering works have been carried out in the early eighties. They gave rise to significant discrepancies, due both to the quality of the sample and to charging problems. This has relevant consequences concerning the application of model systems in terms, e.g., of the magnitude of the correlation energy and the charge transfer energy . On the other hand, very recently the possibility of growing well characterized NiO(100) monocrystalline thin films has shown up. This is achieved by evaporation of Ni in an O@sub 2@ atmosphere onto Ag(100), whose lattice parameter agrees with that of NiO. We have therefore measured IPE spectra of NiO(100) thin films (up to about 50 monolayers) grown by such a method. By studying the dispersion behavior of the various IPE features we were able to classify them as d- or sp-derived states and a d-like ligand hole structure at high energy is clearly shown. By combining these results to X-ray photoemission spectroscopy taken on the same surfaces we find that the magnitude of the gap is similar to what previously found. A new aspect is instead related to the position of the Fermi level (E@sub F@) which is near the middle of the gap. This is at variance with previous results which showed a strong pinning of E@sub F@ at the top of the valence band and were interpreted in detail as an intrinsic effect of "pure" NiO.

10:00am **SS1-TuM6 Surface Structures of Ultrathin Vanadium Oxide Films on Pd(111)@footnote *@**, ***S. Surnev,*** Karl-Franzens-Universität Graz, Austria; *G. Kresse,* Universität Wien, Austria; *M.G. Ramsey, F.P. Netzer,* Karl-Franzens-Universität Graz, Austria

The growth and the atomic structure of epitaxial vanadium oxide thin films on Pd(111) have been investigated by scanning tunnelling microscopy (STM) and low-energy electron diffraction (LEED), combined with ab-initio density-functional theory (DFT) calculations. At submonolayer coverage a well ordered (4x4) oxide overlayer forms which transforms into a porous oxide network with an internal (2x2) periodicity upon exposure with H@sub 2@ at room temperature. The reactivity of the (4x4) phase towards H@sub 2@ is very high, so that small amounts of H@sub 2@ from the residual atmosphere are often sufficient to promote this transformation. The (2x2) phase represents an interface-stabilised surface-V@sub 2@O@sub 3@ layer, which becomes compact upon mild annealing in vacuum exhibiting a (2x2) honeycomb structure. Between 0.5 and 1.0 monolayer equivalents (MLE) the growth of oxide islands with a zigzag stripe structure is observed along with the (2x2) layer. At 1 MLE several VO@sub 2@-like phases are coexistent at the surface in the form of islands with rectangular and hexagonal structures, which are distinguished from the known bulk-type rutile VO@sub 2@ lattice. The detailed atomic structure and energetic stability of these monolayer V-oxide phases have been revealed by the DFT calculations. Above 2 MLE three-dimensional crystallites grow epitaxially on Pd(111) with the corundum structure, which is typical of the bulk-type V@sub 2@O@sub 3@. Two stable V@sub 2@O@sub 3@(0001) terminations have been found in the STM images, which are due to bulk-type oxygen planes and terminal vanadyl species, as suggested by the DFT calculations and confirmed by HREELS. @FootnoteText@ @footnote *@ Supported by the Austrian Science Foundation.

11:00am **SS1-TuM9 Dissociative Adsorption of NO on TiO@sub 2@ (110) Surfaces**, ***J. Abad,*** *O. Böhme, E. Roman,* Institute of Materials Science of Madrid, Spain

The interaction of NO with stoichiometric and defective TiO@sub2@ (110) surfaces has been studied by x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), Auger electron spectroscopy (AES), electron energy loss spectroscopy (EELS) and low energy electron diffraction (LEED). Surfaces with different degree of defects have been characterized monitoring the evolution of the electronic surface structure, with the aim to study the influence of the surface defects on the interaction with NO. The interaction was studied for exposures up to 500L. However, the main effects occur already in the first 2L. The exposure of the surfaces to NO resulted in healing of defect sites without nitrogen adsorption.

11:40am **SS1-TuM11 Investigation of Internal Interfaces: Characterization of Structure, Chemistry, and Relative Adhesion at Metal-Ceramic Interfaces**, ***E.A.A. Jarvis***[1], *E.A. Carter,* University of California, Los Angeles

Reliable, detailed characterization of internal interfaces has become a topic of increasing interest over the past decade. Naturally, both fundamental scientific interest and a wide variety of applications may benefit from improved understanding of heterogeneous interfaces. We employ pseudopotential, planewave density functional theory to investigate local structure and chemistry at several metal-ceramic interfaces. The particular systems under investigation may hold implications for technological advancement of thermal barrier coatings for jet engine turbines. Specifically, we study interfaces between nickel "alloys" and zirconia as well as the nickel-silica interface. By selectively varying the composition of the metal alloy we compare relative adhesion at these interfaces. Our

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[1] **Morton S. Traum Award Finalist**

results indicate that inclusion of early transition metals (Group III and IV) at the nickel-zirconia interface may dramatically increase the interface adhesion strength. The potential application of silicon additions designed to form protective oxides on nickel alloys is discussed in light of our predicted behavior of such interfaces under high temperature conditions similar to those anticipated in jet engine turbine applications. For all systems studied, we analyze the geometric structure and the behavior of the valence electron density to provide insight into the bonding character as well as the trends in adhesion at these interfaces.

Surface Science
Room 122 - Session SS2-TuM
Water at Surfaces

Moderator: E.M. Stuve, University of Washington

8:20am **SS2-TuM1 A Molecular Beam Study of Water Adsorption, Desorption, and Clustering on Pt(111)***, **J.L. Daschbach**, B.M. Peden, G. Teeter, R.S. Smith, B.D. Kay,* Pacific Northwest National Laboratory

Adsorption, desorption, and clustering are investigated by molecular beam techniques. Specular He atom scattering is used to probe the sub-monolayer H2O surface coverage on Pt(111) over the temperature range 22K to 185K. Structural rearrangements of H2O adsorbed at 22K are studied as a function of initial coverage and temperature in the coverage range from 0.01 ML to 1.0 ML by measuring the specular He intensity using linear temperature ramps in the range 0.1 K/s to 10 K/s. Either or both of two transitions are observed depending on coverage, with the first corresponding to the onset of surface diffusion and trapping of mobile H2O by step edges or defects, and the second corresponding to Oswald ripening of 2-D condensed phase islands. Adsorption and desorption kinetics are interrogated isothermally by measuring the H2O coverage in time as a function of H2O beam flux and temperature. At temperatures between 150 K and 165 K the adsorption and desorption spectra are linear in time and therefore independent of coverage. In this region the desorption kinetics are strictly zero-order and can be measured with high precision. The zero order kinetics are a consequence of the existence of a 2-D two phase H2O system present on the Pt surface. At temperatures above 172 K, depending on flux, a transition to non-zero order kinetics is observed with the kinetics consistent with first order. This transition occurs when the system has moved from a two-phase coexistence region to a single phase 2-D gas.

8:40am **SS2-TuM2 Water/MgO Interactions after High Temperature Annealing***, **C.J. Hirschmugl**, M. Harland,* University of Wisconsin-Milwaukee*; R. Plass,* Sandia National Laboratories*; K. Rewolinski, M. Gadjardziska-Josifovska,* University of Wisconsin-Milwaukee

Infrared transmission measurements of MgO(100) and MgO(111) samples as a function of annealing (between 900-1500K) and exposure to air, reveal strikingly different absorption signatures. The measurements are taken 30 degrees from normal incidence to couple to vibrations of adsobates perpendicular and parallel to the surface. Previously, it has previously been surmised that MgO(111) samples annealed to 1500 K undergo a reconstruction at the surface, while MgO(100) does not undergo any similar reconstruction. Notably, the infrared absorption observed for both terminations of MgO(100) and (111) were similar. Samples annealed to 900 K show broad water absorption bands between 3400-3600 cm@super -1@, corresponding to a layer of hydrogen bonded water at the surface. However, this prominent feature disappeared for samples annealed to 1500 K, and a series of weak, sharper bands appeared over the same frequency range. An examination with D@sub 2@O will be used to identify the nature of the bands due to interaction between MgO and water.

9:00am **SS2-TuM3 Morphology of Vapor-Deposited Ice at Low Temperatures by Atomic Force Microscopy***, **S.C. Fain**,* University of Washington*; J.M.K. Donev,* University of Washington and Pacific Northwest National Laboratory*; S.A. Joyce,* Pacific Northwest National Laboratory

Atomic force microscopy (AFM) is being used to study the morphology of multilayer films of vapor-deposited water ice on various substrates as a function of deposition and annealing temperatures below 150K. These experimental studies are coordinated with theoretical studies by other investigators to provide improved understanding of ice growth and properties of ice for use in other fields. For example, nucleation and growth of crystalline ice particles in the upper atmosphere is of central importance for cloud formation, global energy balance, and dynamics of ozone depletion. For these experiments the films are deposited in-situ in ultra-high vacuum from an effusive doser at an angle of 67 degrees from the surface normal. The first measurements were made for ice films deposited on Au(111) on mica. These films were profiled by a probe tip attached to a quartz crystal (Omicron needle sensor) which provides nanometer resolution of surface features. Films deposited below 100K appear relatively flat, adopting the surface texture of the Au(111) substrate. Three-dimensional clusters typically 30 nm high form after annealing these films up to 130K. The lateral dimensions of the clusters depend on the initial coverage. These changes are produced by surface diffusion producing a non-wetting film. The rearrangement happened even if the annealing was done without imaging. Previous thermal desorption measurements by Kay and coworkers [J. Chem. Phys. 91, 5120-5121 (1989) and Surface Science 367, L13-L18 (1996)] have inferred amorphous ice clusters surrounded by bare substrate for films deposited on Au(111) at low-temperatures. Further measurements are in progress using non-contact AFM (Omicron beam-deflection) with the same deposition geometry and different substrates. Supported by Department of Energy's Office of Biological and Environmental Research, a U. W. Nanotechnology Fellowship Award to J.M.K.D., and NSF KDI 99-80125.

9:20am **SS2-TuM4 Initial Growth of Water on Ru(001) and Cage Formation of CD@sub 3@Cl***, **Y. Lilach**, V. Buch, M. Asscher,* The Hebrew University, Israel

The adsorption of H@sub 2@O on Ru(001) and the coadsorption system H@sub 2@O+CD@sub 3@Cl/Ru(001) were studied using Temperature Programmed Desorption (TPD) and work function change (@DELTA@@PHI@) measurements. We developed a kinetic model that fits the measured @DELTA@@PHI@ upon water adsorption at 80K. The model indicates that at very low coverages water monomers dominate, while as coverage increases di- tri- and tetramers are formed. Water tetramers were observed recently by IR measurements to be the dominant species in similar adsorption conditions. The effective @DELTA@@PHI@ contribution of these species suggests an adsorbed cyclic tetramer, with inclined water dipoles. Molecular Dynamics (MD) simulations using the TIP4P potential energy surface for the water-water interaction, were performed as a means for gaining deeper insight into the experimental results. The effective dipoles of the small clusters obtained from the MD simulations were in good agreement with the dipoles predicted by the kinetic model. Adsorbed CD@sub 3@Cl molecules were found to be compressed and then caged under H@sub 2@O layers, as indicated by complex @DELTA@@PHI@ curves monitored upon adsorption. These are explained by the following sequence (a) H@sub 2@O molecules initially compress CD@sub 3@Cl into separate islands. Desorption from this stage suggests that the structure of methyl chloride resembles that of multilayer CD@sub 3@Cl, namely chlorine down in the first layer, while in the second layer it flips up. (b) Hydrophobic displacement of CD@sub 3@Cl from surface sites to become trapped within the water layer. Further increase of the water coverage produces a tight cage of the CD@sub 3@Cl molecules inside the ice structure, as indicated by a sharp, explosive desorption at 165 K.

9:40am **SS2-TuM5 Using Nanoscale Amorphous Films to Study Mixing, Transport and Phase Separation in Deeply Supercooled, Metastable Binary Solutions of Methanol, Ethanol, and Water***, **P. Ayotte**, Z. Dohnalek, G.A. Kimmel, R.S. Smith, B.D. Kay,* Pacific Northwest National Laboratory

The relatively large diffusivities exhibited by amorphous deposits of water, methanol, and ethanol at cryogenic temperature (<160K) opens up the possibility to investigate liquid-phase kinetics in the deeply-supercooled, metastable thin film regime. Compositonally tailored, multilayer films grown by molecular beam dosing techniques are particularly well suited for the characterization of diffusion and desorption kinetics as shown previously for thin film water. While it is well-known that liquid mixtures of alcohol and water exhibit non-ideal solution behavior due to hydrophobic solvation, the complexity of their liquid-solid phase diagrams has been interpreted in terms of formation and decomposition of different crystalline hydrates (stochiometric and/or clathrates). We use molecular beam scattering and programmed desorption (both TPD and isothermal) to study the desorption and mixing kinetics as well as the crystallization of mixed multilayer ices of water, ethanol, and methanol. The desorption spectra exhibit complex features that depend strongly on both the film's composition and thickness. Analysis of the desorption spectra using a kinetic model that describes liquid solution evaporation reveals both the extent of mixing and the details of the solvation kinetics in the metastable liquids. We compare these results with existing liquid-solid phase diagrams for these binary mixtures. While thin binary films of methanol and ethanol exhibit ideal behavior, binary mixtures of water and either alcohol display strongly non-ideal behavior presumably caused by precipitation of solid crystalline hydrates from the deeply-supercooled, metastable liquid solutions. @FootnoteText@ P. Ayotte is an NSERC Postdoctoral Fellow. Pacific Northwest Laboratory is a multiprogram National Laboratory operated for the U. S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

10:00am **SS2-TuM6 Crystallization Kinetics of Amorphous Solid Water on Hydrophobic and Hydrophilic Substrates*, G. Teeter*,** *Z. Dohnalek, R.S. Smith, G.A. Kimmel, B.D. Kay,* Pacific Northwest National Laboratory

The crystallization kinetics of thin film (5-200 BL) Amorphous Solid Water (ASW) has been studied using Temperature Programmed Desorption (TPD) and Fourier Transform Infrared Spectroscopy (FTIR). ASW thin films were deposited by molecular beam on clean, w ell-ordered Pt(111) and decane (C@sub 10@H@sub 22@) thin film substrates in order to probe the dependence of H@sub 2@O crystallization kinetics on substrate-H@sub 2@O interactions. H@sub 2@O wets the Pt(111) surface and is non-wetting on the decane substr ate. In both cases crystallization of the ASW thin film proceeds via nucleation and 3D growth of the crystalline phase. As-deposited ASW kinetically wets the decane substrate at low temperature, but TPD and FTIR results indicate that crystallization is accompanied by de-wetting the H@sub 2@O film from the decane substrate. Details of the experimental techniques, results, and implications will be presented.t. @FootnoteText@ Pacific Northwest National Laboratory is a multiprogram National Laboratory operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830. a.

10:20am **SS2-TuM7 A Two Step Dissociative Ionization and Desorption Mechanism for Water Ion Cluster Emission from a Pt Field Emitter Tip*, C.J. Rothfuss*,** *V.K. Medvedev, E.M. Stuve,* University of Washington

Our recent work on the behavior of water molecules adsorbed on a Pt emitter tip in high fields (~1 V/ Å) has provided an understanding of the behavior of water dissociation and ion cluster [H@super +@(H@sub 2@O)@sub n@] emission. Water ion emission from an emitter tip has traditionally been treated as a single step event. While differing n cluster types have been observed, typically ranging to 10 or above, no detailed explanation of the mechanism for cluster formation has been suggested. Mass resolved ramped field desorption experiments from field adsorbed water layers (T>170K) have given field dependencies for specific ion cluster masses. As the field was ramped, each cluster type was observed, in turn, beginning with high n clusters and transitioning to lower n clusters. The emission of high n clusters was energetically favored, while low n clusters were favored kinetically. However, at low temperatures (T

10:40am **SS2-TuM8 Bonding of Water to Metal Surfaces Studied with Core-level Spectroscopies*, H. Ogasawara*,** *D. Nordlund,* Uppsala University, Sweden*; B. Brena,* University of Stockholm, Sweden*; L.-Å. Näslund, M. Nagasono,* Uppsala University, Sweden*; L.G.M. Petterson,* University of Stockholm, Sweden*; A. Nilsson,* Uppsala University, Sweden and Stanford University, Sweden

The chemical interaction between water and a metal surface is important in many practical fields, including corrosion, electrochemistry, molecular environmental science and heterogeneous catalysis. On smooth metal surfaces, (e.g. fcc(111) or hcp(0001)), water molecules adsorb intact with strong intermolecular forces between the water molecules. This leads to the formation of a hexagonal two-dimensional ice lattice proposed as a "bilayer structure".@footnote 1@ The unit cell contains two water molecules, which are different in the interaction with respect to the metal surface. We have studied the water "bilayer structure" on Pt(111) with X-ray absorption and X-ray emission spectroscopies. These two techniques provide atom specific information about electronic structure. We have identified two different water-metal chemical bonds in the "bilayer structure". @FootnoteText@ @footnote 1@ P.A. Thiel and T.E. Madey, Surface Science Reports 7, 211 (1987).

11:00am **SS2-TuM9 The Interaction of Carbon Monoxide with Hydrogen-bonding Molecular Ice Surfaces**, *J.W. Dever, M.P. Collings,* ***M.R.S. McCoustra,*** University of Nottingham, UK

Carbon monoxide (CO) is the second most abundant molecule in the Universe after hydrogen. It's interaction with solid grain surfaces is key therefore to understanding gas-grain interactions in the interstellar medium, whether those interactions relate to the freezing out of molecules on grains in cold, dark molecular clouds or their eventual reappearance in the gas phase and their role in radiative cooling of warm, collapsing proto-stellar objects. Using a combination of temperature programmed desorption (TPD) and reflection-absorption infrared spectroscopy (RAIRS), we have conducted state-of-the-art surface physicochemical studies of the interaction of CO with hydrogen-bonded molecular ice (water, ammonia and methanol) surfaces that represent a model of the surfaces of some types of interstellar grains. We will present the results of these first detailed ultrahigh vacuum studies of realistic gas-grain interactions and their interpretation in terms of simple models of the CO-ice interaction.

11:20am **SS2-TuM10 Water Reactivity with MgO(100)Thin Film Surfaces Studied by Electron Stimulated Desorption***, D. Cáceres, I. Colera, I. Vergara, R. González,* Universidad Carlos III de Madrid, Spain*; E.L. Román,* ***J.L. de Segovia***, CSIC, Spain

The adsorption of two isotopic forms of water, D@sub 2@ @super 16@O and H@sub 2@ @super 18@O, with well characterised MgO(100) thin film surfaces at 300 K was studied by Electron Stimulated Desorption, ESD. Oriented MgO(100) thin films were grown on Si(100) at 940 K by rf-sputtering with a Mg target and at a total pressure of 7 x 10@super -3@ mbar (10% O@sub 2@ and 90% Ar). These films were characterized by X-Ray diffraction, Auger Electron Spectroscopy (AES), X-Ray Photoelectron Spectroscopy (XPS), and Electron Energy Loss Spectroscopy (EELS). Previous ESD results@footnote 1,2@ of O@super +@ desorbed species from clean surfaces of bulk MgO(100) showed a bimodal energy distribution structure with peaks at 6 and 9 eV. Their origin was assigned to O@super +@ desorption from surface defects and to desorption from the oxide, respectively. The aim of the present ESD study of MgO(100) thin films is twofold: (i) to compare the previous results on bulk defective surfaces (stepped or with oxygen vacancies) with a thin film surface with no steps, and (ii) to study the reactivity of water with these thin films, and the influence of surface defects on the hydrolisis processes. D and @super 18@O isotopes were used to distinguish them from the H contamitation and from the @super 16@O of the oxide, respectively. Ion yield experiments using H@sub 2@ @super 18@O show @super 18@O@super +@ and @super 18@OH@super +@ desorbed ions in addition to the usual H@super +@ and @super 16@O@super +@ ions. The adsorption of @super 18@O is related to the @super 16@O defective sites on the MgO(100) thin films. Preliminary results indicate that the Feibelman-Knotek mechanism is responsible for the desorption processes. Ion kinetic distribution curves at different electron energies are also discussed. @FootnoteText@@footnote 1@ I. Colera, E. Soria, E. Rom@aa a@n and R. Gonz@aa a@lez, Vacuum 48 nº 7-9 pag 647 to 649 (1997) @footnote 2@ I. Colera, R. González, E. Soria, J.L. de Segovia, E.L. Román and Y. Chen, J. Vac. Sci. Technol. A 15(3) pag 1698-1703 (1997).

11:40am **SS2-TuM11 The Influence of Calcium Carbonate Coatings on Contamination Reactivity***,* ***T. Droubay***, *S.A. Chambers,* Pacific Northwest National Laboratory

High energy-resolution x-ray photoemission spectroscopy (XPS) is used in conjunction with scanning probe microscopy to investigate the influence of calcium carbonate coatings on the adsorption of aqueous CrO@sub 4@@super 2-@ on epitaxial Fe@sub 3@O@sub 4@/MgO(001) surfaces prepared by oxygen plasma assisted molecular beam epitaxy (OPA-MBE). Deposition of calcium carbonate films was accomplished with the use of a polymer-induced liquid-precursor (PILP) process, which utilizes polyaspartate to suppress growth of crystal aggregates and results in the formation of flat films. Of the three polymorphs of CaCO@sub 3@, the films primarily consist of a combination of vaterite and calcite with undetectable amounts of aragonite. X-ray photoemission analysis and atomic force microscopy reveal a thin polymer interfacial layer between the underlying Fe@sub 3@O@sub 4@ and carbonate overlayer which acts as a template for vaterite growth. An increase of the intensity in the low binding energy shoulder of the Fe 2p@super 3/2@ core-level and a decrease in the Fe(III) non-charge transfer satellite is evidence of an increase in Fe(II) at the magnetite surface as a result of the aqueous growth environment. This result is consistent with surface reduction found during the interaction of Fe@sub 3@O@sub 4@/MgO(001) with liquid water. The effects of carbonate coating on substrate reactivity, emphasizing electron transfer reactions responsible for the reductive immobilization of Cr(VI)O@sub 4@@super 2-@ will be discussed. These results have application in chromate remediation efforts centered on the reduction of chromate contamination by Fe(II).

Thin Films
Room 123 - Session TF-TuM
Optical Thin Films

Moderator: J. Verhoeven, FOM Institute, The Netherlands

8:20am **TF-TuM1 Influence of Processing Conditions on Sputter Deposited ZnO:Al Thin Films*, L.W. Rieth,*** *P.H. Holloway,* University of Florida

Thin films of zinc oxide (ZnO) are useful in many applications including transparent conductors, gas sensors, RF filters, varistors, and Cu(In,Ga)Se@sub 2@ (CIGS) based thin film solar cells. Thin films of Al doped ZnO are deposited from a ceramic target of ZnO:Al@sub 2@O@sub 3@ (98wt%:2wt%) using an 8 inch RF diode source onto cleaned soda-lime glass substrates with no intentional heating. RF power and process pressure are varied over the ranges of 250 - 1000 watts and 5 - 50 mTorr, respectively. As deposited and modestly heat treated films (400°C for 1 hour) are characterized by atomic force microscopy (AFM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), four point probe, Hall measurements, and spectrophotometry. AFM micropgraphs indicate the films are polycrystalline with grain sizes between 10 and 100nm. XRD results indicate the films have the wurtzite structure with a strong basal texture (0001). XPS spectra reveal the films have the proper stoichiometry, and a chemisorbed surface oxide species that is sensitive in particular to the gas ambient during the modest heat treatments. Electrical data show that the films have a large range of resistivities, which improve with heat treatment to as low as 10@sup -3@ @ohm@-cm, while maintaining transmission greater than 80% across the visible range. The properties were sensitive to location on the substrate relative to the sputter deposition source, exhibiting the lowest resistivity for off axis deposited films These results are discussed with respect to the hypothesis that negative ion resputtering (NIR) strongly influences the properties of the deposited films.

8:40am **TF-TuM2 Linear Combinatorial Synthesis of Cadmium Tin Oxide Films by Low-pressure Chemical Vapor Deposition*, X. Li,*** *T. Gessert, T. Coutts,* National Renewable Energy Laboratory

Recent work on transparent conducting oxides (TCOs) such as tin oxide (SnO@sub 2@) and cadmium stannate (CTO) has been of great interest because of the relevance of these materials to important technological applications. The electrical and optical properties of these materials are relevant to low-emissivity glass, flat-panel displays, and thin-film solar cells. SnO2 is very durable and appropriate for coatings on low-emissivity windows whereas CdO has exhibited mobilities over 200 cm@super 2@ V@super -1@ s@super-1@. The intermediate alloy, CTO, may be either orthorhombic or spinel, although thin-films are typically spinel. This material has also exhibited high mobilities of 80 cm2 V-1 s-1, although requiring rather specific deposition and annealing conditions. This paper will discuss our early efforts to make this material using a technique that is potentially more suitable for large-scale manufacture. We have deposited films of the individual materials using low-pressure metal organic chemical vapor deposition (LPMODVD) and have also combined the precursors to make films of CTO. We used tetramethyltin (TMT), dimethylcadmium and oxygen as the precursors. The concentrations of the two organic precursors varied along the length of the substrate because of their varying rates of decomposition. In effect, we had established conditions that enabled us to perform linear combinatorial synthesis experiments. Our objective was to make CTO films but the films varied from near-CdO (at the leading edge of the substrate) to near-SnO2 (at the trailing edge). The mobilities varied from less than 1 cm2 V-1 s-1 to about 60 cm2 V-1 s-1. Optical data indicated that the bandgaps varied from 2.75 eV (somewhat characteristic of CdO) to about 3.65 eV (more characteristic of SnO2). We also measured the compositional and structural variations along the length of the substrate and found consistent behavior. Within a limited range of distances, we established material similar to spinel CTO.

9:00am **TF-TuM3 Challenges in the Development of Novel Transparent Conducting Oxides*, T. Coutts,*** *D.S. Ginley, D.L. Young, X. Li, J.D. Perkins,* National Renewable Energy Laboratory **INVITED**

Transparent conducting oxides (TCOs) have been used extensively during the last forty years for a variety of applications including, flat-panel displays, photovoltaic modules, and heat-conserving infrared reflectors on windows. While their performance has been acceptable for these applications, the demands of new developments and the emergence of new applications indicate that this will change in the near future. Changes in the quality of existing TCOs and/or the development of new materials are, therefore, certain to be required. In this paper, we shall review our work at the National Renewable Energy Laboratory in this field. This includes the synthesis of high quality spinel n-type TCOs such as cadmium and zinc stannate, binary oxides of tin, zinc and cadmium, and exploratory research into p-type TCOs such as ZnO:NO and the delafossites CuAlO@sub 2@ and CuInO@sub 2@. Several deposition techniques such as sputtering, pulsed laser deposition, and chemical vapor deposition are used, with combinatorial synthesis, to facilitate investigation of the vast phase-space encompassed by TCOs. In addition, we have extensive methods of characterizing the electrical, compositional, structural and crystallographic properties of the materials of interest.

9:40am **TF-TuM5 Kinetics of Hydrogen Induced Changes of Optical Properties in Smart Coatings*, M. Wuttig,*** Aachen University of Technology, Germany

Certain transition metal oxides and hydrides show remarkable changes of their optical properties upon hydrogen exposure, in particular if the film surface is covered by a thin Pd or Pt film. This effect can be used to create window coatings that enable a switching of optical properties. In this study we compare the switching kinetics of several thin film systems including Mg, Gd, MgGd alloys and WO@sub 3@ upon hydrogen exposure. The switching process is studied in-situ by time resolved optical spectroscopy measurements, x-ray diffraction and x-ray reflection as well as mechanical stress measurements. The latter measurements reveal that for the different materials very different stresses arise as a function of hydrogen exposure. The lowest stresses are observed for WO@sub 3@ films, while stresses above 1 GPa were observed for Gd. Nevertheless the value of the stress change alone is insufficient to determine if plastic deformation and degradation of the films upon hydrogen exposure takes place. The influence of the film morphology on switching kinetics is carefully studied. A particularly pronounced correlation between switching kinetics and film density is observed for the WO@sub 3@ films where the time constant varies by more than two orders of magnitude upon a variation in density by 20%.

10:00am **TF-TuM6 Plasma Enhanced Chemical Vapour Deposition of SiO@sub x@N@sub y@ for Large Area Applications in a Matrix Distributed Electron Cyclotron Resonance Reactor*, A. Hofrichter,*** *A. Charaya, B. Drevillon,* Ecole Polytechnique CNRS, France

There is a considerable interest to use high-density plasma sources for plasma enhanced chemical vapor deposition of thin films on large areas. Major issues in this field are deposition uniformity and whether the use of radiofrequency bias is needed to obtain high quality materials. In this work we use the recently developed matrix distributed electron cyclotron resonance concept for the deposition of silicon oxynitride thin films. By using an array of individually tunable ECR plasma sources (5x5 in our case), this concept is easily scaleable by increasing the number of the sources while maintaining the necessary plasma homogeneity. Films were deposited onto glass, crystalline silicon and polycarbonate substrates with a typical uniformity of 1,5 % on 200x200 mm, and 4% on 350x350 mm. The properties of the materials are analyzed with in situ UV-Visible spectroscopic phase-modulated ellipsometry (PME), ex-situ transmission, Infra-Red ellipsometry, RBS and ERDA measurements. Without substrate heating and radiofrequency bias dense, non-absorbing, low hydrogen content stoichiometric films of SiO@sub 2@ and Si @sub 3@N@sub 4@ are grown from the mixture of SiH@sub 4@, O@sub 2@ and N@sub 2@. By changing the nitrogen to oxygen gas flow ratio the refractive index (measured at 632.8 nm) can be smoothly and reproducibly tuned from 1.46 to 1.95. Deposition rates are between 13.0 and 0.5 nm/s for SiO@sub 2@ and Si@sub 3@ N@sub 4@ respectively. The influence of process parameters, such as deposition pressure, microwave power, gas flows and flow ratios are studied and correlated with Langmuir probe measurements and optical emission spectroscopy to obtain better insight into the plasma properties and the mechanisms of the growth.

10:20am **TF-TuM7 High Growth Rate Deposition of a-SiN@sub x@:H Films for Photovoltaic Applications*, J. Hong,*** Eindhoven University of Technology, The Netherlands*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands*; F.J.H. Van Assche,* Eindhoven University of Technology, The Netherlands*; D.C. Schram,* Eindhoven University of Technology, The Netherlands, Netherlands*; M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands

A new technique has been developed for the deposition of amorphous silicon nitride (a-SiN@sub x@:H) films at deposition rates up to ~200 Å/s by injection of SiH@sub 4@ into an expanding Ar/H@sub 2@/N@sub 2@ plasma. This so-called expanding thermal plasma (ETP) technique is relevant for high-throughput deposition of a-SiN@sub x@:H anti-reflection

(AR) coatings on industrial Si solar cells, where the a-SiN@sub x@:H can simultaneously lead to both bulk and surface passivation. Silicon nitride films with different Si/N ratios and hydrogen concentrations have been deposited on different types of Si solar cells. It has been revealed that the optical properties can be fully tuned to obtain an optimized AR matching with the Si substrate while real-time ellipsometry is used as feedback during processing. Film homogeneity measurements revealed less than 5% variation over 10x10 cm@super 2@ cells. Bulk passivation of multi-crystalline Si cells has been suggested by an enhanced red response of the coated cells, although preliminary results on surface passivation have not yet revealed sufficient reduction of the surface recombination on mono-crystalline Si cells. More data on real solar cells will be presented. The plasma chemistry has been studied by threshold ionization mass spectrometry and cavity ring down spectroscopy. These measurements suggest the creation of SiH@sub 3@ radicals by atomic H from the plasma source leading to a neutral-dominated deposition of a Si top layer, followed by subsequent nitriding by atomic N. Real-time attenuated total reflection infrared spectroscopy is applied to extend the insight into this deposition mechanism.

10:40am **TF-TuM8 Electrical Characteristics and Growth of ZrO@sub2@ as a Gate Dielectric***, **Y. Kim**, Y. Kim, H. Jeon,* Hanyang University, Korea

We have studied ZrO@sub 2@ thin film as an alternative gate dielectric. It was deposited on a Si substrate by RF reactive sputtering system which was optimized to achieve high quality thin film. O@sub 2@ flow and power were modulated to control the interface quality and growth rate. This ZrO@sub 2@ thin film was annealed from 600 °C to 900 °C for 30 sec with rapid thermal annealing (RTA).@footnote 1@ Pt was deposited as a top electrode for metal-oxide-semiconductor (MOS) capacitor by ultra high vacuum evaporation system and this capacitor was annealed at 450 °C for 30 sec with RTA in H@sub 2@ + N@sub 2@ ambient. Capacitance-voltage measurements showed an equivalent oxide thickness of less than 30 Å with no significant dispersion of the capacitance for 1MHz frequency. Current-voltage measurements exhibited the low leakage current at -1.0V. Hysteresis shift in these films was measured to be less than 100mV. Interface state density and reliability were measured. We examined cross-sectional transmission electron microscopy and X-ray diffraction to observe reaction and crystallization of zirconium oxide.@footnote 2@ We also examined the zirconium oxide formation depending on the annealing temperature by in-situ Auger electron spectroscopy system connected with ultrahigh vacuum furnace. @FootnoteText@ @footnote 1@B. H. Lee, L. Kang, R. Nieh, W. Qi, and J. C. Lee, Appl. Phys. Lett., vol. 76, p. 1927, Apr. 2000. @footnote 2@G. D. Wilk and R. M. Wallace Appl. Phys. Lett., vol. 76 p. 112, Jan. 2000.

11:20am **TF-TuM10 Effect of Cation Charge State and Site Occupancy on the Dielectric Response of ITCO Spinel Films***, **C.F. Windisch Jr.**,* Pacific Northwest National Laboratory*; K.F. Ferris,* Pacific Northwest National Laboratory, us*; G.J. Exarhos,* Pacific Northwest National Laboratory

Cobalt-nickel oxide thin films have recently showed promise as infrared transparent conducting oxide (ITCO) materials. In this work, nominal 100 nm thick films with electrical resistivity on the order of 10@super -3@ ohm cm were prepared using both solution and rf magnetron sputter deposition techniques with subsequent post-deposition annealing in air. A combination of XRD, XPS, UV/Vis, Raman spectroscopy, Hall and Seebeck measurements confirmed that a spinel oxide is the primary conducting component of these films and that the conductivity is maximum at or near the NiCo@sub 2@O@sub 4@ stoichiometry, where x = Co/(Co + Ni) = 0.67. Between x = 0.67 and 1.0, i.e. Co@sub 3@O@sub 4@, the conductivity decreases by many orders of magnitude. As x decreases (higher nickel content), conductivity improves somewhat until phase instability drives precipitation of nickel oxide with concomitant loss in conductivity. The reason for this variation has been the subject of much debate in the literature with important questions still unresolved. In this paper, we show, by careful analysis of the XPS and Raman spectra, that the charge state and site occupancy distribution of the Ni cations, as well as the defect structure involving singly charged oxygen anions, vary predictably with composition and conductivity. Electronic structure modeling studies performed in conjunction with the spectroscopy experiments provide a fundamental perspective on the relationship between the optical response and attendant conductivity for this important new class of TCO materials that are being investigated for prospective use in optical limiting and switching applications. This work was conducted under the "Electroactive Coatings and Shutters for Protection of Sensors" Program funded through DARPA contract DAAD19-99-1-0003. Pacific Northwest National Laboratory (PNNL) is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

11:40am **TF-TuM11 Multi-layer Chromium-based Optical Coatings for 157nm Lithography***, **P.D. Rack**, B.W. Smith, A. Bourov, D. Baiko,* Rochester Institute of Technology*; M.G. Lassiter,* Photronics Corp.

Chromium based multi-layer films have been the dominant masking material for optical microlithography. The next generation optical lithography exposure wavelength is expected to be 157nm from an F2 laser source. Of critical interest for this exposure wavelength is the optical properties of the chromium multi-layer mask. Traditionally the masking film has been ~100-120 nm thick, however for accurate critical dimension control for off-axis illumination sources, it is desirable to thin the masking film thickness. To design a process to deposit a thinned masking material, the composition of the standard masking material was initially confirmed via x-ray photoelectron spectroscopy depth profiling. The composition of the film was determined to be a CrxNy film with a graded CrxOyNz anti-reflecting top layer. To evaluate the thinned materials, a design of experiments was performed to reactively sputter a metallic chromium target in an Ar-N2 and an Ar-N2-O2 ambient, respectively. After successfully reproducing the ~120nm thick multi-layer film, a series of scaled films with a total thickness of 50 and 80 nm were deposited. Vacuum ultra violet (VUV) transmission, reflection, and spectroscopic ellipsometry measurements were performed on each film and the optical constants (n and k) of the individual layers were determined. Finally, the entire multi-layer film stack was modeled with an effective medium approximation and found to correlate well with the experimental reflection and transmission data. In this presentation, we will discuss reactive sputter deposition metallic chromium to form the CrxNy/CrxOyNz multi-layer thin films. The optical characterization results will be presented and discussed in regard to the reflection and optical density requirements necessary for a masking material. Finally the modeling of the spectroscopic ellipsometry will be presented and the effective media approximation of the film stacks will be discussed.

Vacuum Science & Technology
Room 125 - Session VST-TuM

Turbomolecular, Molecular Drag and Similar Pumps

Moderator: R.G. Livesey, BOC Edwards

8:20am **VST-TuM1 History of Alcatel Turbomolecular Pump Development***, **R. Mathes**, O. Boulon,* Alcatel Vacuum Technology, France **INVITED**

This article describes the development of turbomolecular pumps at Alcatel over more than 20 years. It shows the changes from the initial molecular pumps and turbomolecular pumps to the present technology of hybrid turbomolecular pumps. The different bearing technologies used in pumps such as ball bearing, gas bearing and maglev bearing technologies are described. The changes in the rotor design of MDP and TMP are explained by the improvement of calculation methods such as analytical calculation for molecular and viscous flow, Monte Carlo simulation for the molecular flow, direct Monte Carlo simulation for transition flow and simulation with CFD codes for viscous flows in 2D and 3D.

9:00am **VST-TuM3 Effects of Surface Roughness of Blades on the Pumping Performance of a Turbomolecular Pump***, M. Yabuki, **T. Sawada**, W. Sugiyama,* Akita University, Japan*; M. Watanabe,* Osaka Vacuum Ltd., Japan

Turbomolecular pumps (TMPs) are widely used in the semiconductor and other thin film industries. Some semiconductor processes form corrosive gases such as HCl or HF as byproducts. The elements of a TMP are sometimes coated with ceramic (SiO @sub2@) film for the purpose of preventing corrosion on the TMP. The blades coated with SiO@sub2@ have relatively rough surfaces and may change the pumping performance. The effects of the surface roughness of the blades on the pumping performance were studied experimentally and theoretically. First, the maximum-compression ratio was measured for the non-coated TMP that had two rotor discs and one stator disc. Next, the pump that had been tested was disassembled and the elements were coated with SiO@sub2@. Then the maximum-compression ratio was measured for the reassembled-coated pump. The compression ratio attained by the coated pump was compared with the one attained by the non-coated pump. The effects of the surface roughness were also estimated by a two dimensional calculation. Both the experimental and calculated results show that the TMP coated with SiO@sub2@ film gives about a 13% higher maximum-compression ratio than that of the non-coated TMP when the blade speed ratio is 0.47.

9:20am **VST-TuM4 Power Optimisation of a Hybrid Turbomolecular-drag Vacuum Pump***, **S. Giors**, R. Cerruti, J.C. Helmer,* Varian Vacuum Technologies, Italy

Varian has specialised in the development of Gaede stages for extending the tolerable fore pressure of hybrid turbomolecular-drag vacuum pumps. The design of the first hybrid turbomolecular pumps was focused to the optimisation of their vacuum performances, disregarding the power dissipated to get them. The power dissipated by the pump was just a consequence of a given vacuum optimisation, normally resulting in high power dissipation rates. Nowadays, this approach is no more acceptable, as a consequence of our need to build pumps able to reach higher and higher fore pressures. Today the optimisation has to be carried out, taking into account both power dissipation and performance, stage by stage. In a previous paper@footnote 1@ we presented a model able to predict power consumption of a single Gaede stage. Now that model is extended to a cascade of Gaede stages and applied to the optimisation of a full commercial pump. The drag stages of a 250 L/s pump have been redesigned according to that model in order to heavily reduce its power consumption without compromising its vacuum performance and without affecting the production process. Measurements show about 50% in power reduction with respect to the old pump without any loss in pumping speed, compression ratio or high throughput characteristics. This work demonstrates that further improvement is possible in the design of commercial hybrid turbomolecular-drag pumps, in order to reduce power dissipation, and hence cooling requirements, rotor working temperature and reliability. @FootnoteText@ @footnote 1@ R. Cerruti, M. Spagnol, J. C. Helmer, "Power dissipation in turbomolecular pumps at high pressure", J. Vac. Sci. Technol. A 17(5), 3096-3102, Sept/Oct 1999.

9:40am **VST-TuM5 Study on the Performance Prediction of Turbine Blade under Low Vacuum***, **M. Watanabe**,* Osaka Vacuum, Ltd., Japan*; T. Sawada,* Akita University, Japan*; T. Ohbayashi, M. Iguchi,* Osaka Vacuum, Ltd., Japan

A turbo molecular pump with the ability to pump a large quantity of gas under a low vacuum is required in the fields of semiconductor and liquid-crystal device manufacturing. In this study, we propose the method of performance prediction for a turbine blade under a low vacuum, which enables the design of high throughput pump. The performance was analyzed with Stokes equation, which governs the low vacuum flow between the turbine blades with small Reynolds numbers. Experiments were carried out with conventional and optimized blade pumps under a low vacuum; throughputs were measured. The comparison between the measurements and the predicted values showed that the present method predicts the performance of the turbo molecular pump in the pressure range under 10 Pa with a sufficient accuracy for practical applications.

10:20am **VST-TuM7 Turbine-type Pumps in High-vacuum Technology***, **M.H. Hablanian**,* Consultant **INVITED**

High-vacuum pumping technology has undergone a very significant transformation during the last 45 years: from oil vapor-jet pumps (so-called diffusion pumps) and oil-sealed mechanical pumps to a variety of oil-free technologies. The major trend has been the demand for improved cleanliness. Ultrahigh vacuum techniques, ion-getter pumping, cryogenic pumps, turbomolecular pumps, and oil-free roughing pumps are part of the trend. Turbomolecular pumps, or turbopumps, of various designs have become one of the major means of obtaining high vacuum. Their relative simplicity of operation, an advantage of a single rotor, a possibility of use in a remarkably wide range of pressure, and the convenience of multi-staging in a compact body to achieve high compression ratios, combine to provide a design flexibility unrivaled by other types of pumps. The design variations are still in process. Articles describing new designs are appearing in technical journals and patent literature. These include compound pumps, hybrid pumps, pumps with multiple inlets and exhausts, miniature pumps, and finally, pumps that are capable of exhausting directly into atmosphere. The latest addition to the variety of pumping disks, attached to the same shaft, are regenerative-centrifugal impellers. The proper selection and design of such pumping disks has a significant impact on performance and power consumption. We should expect that in the next 10 or 20 years the potential product possibilities should be sorted out.

Applied Surface Analysis
Room 134 - Session AS-TuA

Depth Profiling I

Moderators: S. Hofmann, Max-Planck-Institute for Metals Research, Germany, R.L. Opila, Agere Systems

2:00pm **AS-TuA1 Sputtering-induced Effects in Ultra Shallow Depth Profiling*, A.T.S. Wee,*** National University of Singapore, Singapore*; C.M. Ng, R. Liu,* National University of Singapore **INVITED**

Following the increasingly stringent requirements in the characterization of sub-micron IC devices, a good understanding of various factors affecting ultra shallow depth profiling in secondary ion mass spectrometry (SIMS) becomes crucial. Achieving high depth resolution (of the order of 1 nm) is becoming critical in the semiconductor industry today, and various methods have been developed to optimize depth resolution. In this paper, I will discuss ultra shallow SIMS depth profiling in several important semiconductor systems, namely B delta-doped Si, SiGe heterostructures and ultrathin oxynitride gate films. Results from both dynamic SIMS (Cameca IMS 6f) and TOF-SIMS (ION-TOF IV) will be presented. By using low energy (e.g. 500 eV) O@sub 2@@super +@ and Cs@super +@ beams, the relationship between depth resolution of the delta layers and surface topography measured by atomic force microscopy (AFM) is studied. The effects of oxygen flooding and sample rotation, used to suppress surface roughening, have also been investigated. X-ray photoelectron spectroscopy (XPS) is used to characterize the surface chemical composition of the crater bottom and a direct relationship between the surface chemical state and surface roughness is established. The various factors that limit the depth resolution in ultra shallow SIMS depth profiling are discussed.

2:40pm **AS-TuA3 Low Energy Ion-surface Interactions in Ultrashallow Profiling Investigated with In-situ Medium Energy Ion Scattering Spectroscopy*, D.W. Moon,*** Korea Research Institute of Standards and Science, Korea*; H.I. Lee,* Korea Research Institute of Standards and Science*; H.J. Kang,* Chungbuk National University, Korea

For ultrashallow junction profiling with secondary ion mass spectrometry (SIMS), low energy ions have been used successfully. However, detailed understanding on the low energy ion-surface interactions have been lacking for quantitative ultrashallow junction SIMS profiling. Especially the transient surface sputtering effect in the pre-equilibrium region is one of the important phenomena to be understood. In this report, low energy ion-surface interactions are studied with in-situ medium energy ion scattering spectroscopy (MEIS) which provide quantitative composition and structural information with better than 1nm depth resolution. Damage profiles in Si(100) surfaces due to 100~500 eV O@sub 2@@super+@ ion bombardment were measured with in-situ MEIS as a function of dose, energy, and angle. The thickness of the damaged layer can be decreased down to 1nm with 80° grazing incidence. The transient sputtering yield change of an amorphous Si layer on a Si(100) could be measured quantitatively as a function of the ion dose for normal incident 500 eV O@sub 2@@super+@ ion bombardment. At the initial stage of 500 eV O@sub 2@@super+@ ion bombardment before the surface oxidation, the sputtering yield of Si was 1.4 (Si atoms/O@sub 2@@super+@). With sputtering, the Si sputtering yield decreased rapidly down to 0.06 (Si atoms/O@sub 2@@super+@) at the ion dose of 3x10@super 16@ O@sub 2@@super+@ cm@sub -2@. An initial Si surface swelling was observed due to the higher oxygen incorporation rate than the Si sputtering rate. Transient sputtering yield decrease of Si due to 500eV Ar@super +@ is also observed, in contrary.

3:00pm **AS-TuA4 Low Energy Dual Beam Depth-Profiling: Influence of Sputter- and Analysis-Beam Parameters on Profile Performance using TOF-SIMS*, T. Grehl,*** *R. Moellers, E. Niehuis,* ION-TOF GmbH, Germany

In general TOF-SIMS measurements are carried out in the so-called quasi static mode where the fluence of the analysis beam is so low that the sample damage or the erosion caused by the primary ions is regarded to be negligible. A common way to take depth profiles with a TOF-SIMS instrument is the operation in the so-called dual beam mode. In this mode sample erosion and sample analysis are carried out with two different ion beams. Whereas sample erosion is performed with a quasi DC-beam, the sample analysis is done with a pulsed ion beam of relatively low current density. This mode offers great flexibility to optimize the sputter conditions (i. e. erosion rate, energy, sputter species, angle of incidence, etc.) for the specific analytical task independent from the analytical conditions. Typically sputter ions such as Cs@super +@ or O@sub 2@@super +@ are used to optimize the secondary ion yield. For the sample analysis a Ga liquid metal ion gun with high brightness and high lateral resolution is preferable. This combination is most suitable for applications such as micro area depth profiling or 3D-analysis where the analysis is taken from a small raster field within the sputter crater. Since the contribution of the high energy analysis beam to the atomic mixing becomes more significant for small areas, the influence of the analysis beam on the depth resolution requires a more detailed study. In this paper we investigate how the ion energy of the sputter gun as well as the analysis gun affects the depth profile. The sputter ion energy is varied from 200 eV to 1000 eV for Cs@super +@ as well as for O@sub 2@@super +@ while the erosion rate is kept constant during these measurements. In addition, the current density of the analysis gun will be changed while keeping constant sputter conditions.

3:40pm **AS-TuA6 Reference Materials for SIMS: Philosophy, Development, and Results*, D.S. Simons,*** National Institute of Standards and Technology **INVITED**

NIST has been developing reference materials for calibration of secondary ion mass spectrometers for approximately 10 years. The choice of materials was not only dictated by their potential market and economic impact, but also by the availability of independent analytical methods to perform certification measurements in a traceable manner. For these reasons, a decision was made to target materials of use to the semiconductor industry that were routinely analyzed by SIMS and for which good measurement calibration was important. Specifically, a program was undertaken to produce ion implants of the common dopants boron, arsenic, and phosphorus in silicon. The retained dose of the dopants would be certified by nuclear analytical methods that were available at the NIST research reactor. The first such reference material, SRM 2137, was a @super 10@B implant in Si certified by a neutron reaction method known as neutron depth profiling. Lessons learned in this first project were incorporated into the production and certification by instrumental neutron activation analysis of a @super 75@As implant in Si, SRM 2134. NIST is currently validating certification procedures for a @super 31@P implant in Si by radiochemical neutron activation analysis. We will show examples of the level of improvement in SIMS measurements that has been achieved by use of these reference materials.

Advancing toward Sustainability Topical Conference
Room 111 - Session AT-TuA

Sustainable Climate-Friendly Semiconductor Manufacturing

Moderator: P.J. Maroulis, Air Products and Chemicals, Inc.

3:00pm **AT-TuA4 Sustainable Semiconductor Manufacturing: Methods and Applications to Reduce the Environmental Impact of Chip Making*, S. Raoux,*** *D. Ho, R. Smati, M. Alaoui, P. Porshnev, T. Francis,* Applied Materials

The semiconductor industry is pursuing aggressive programs to reduce the environmental impact of its manufacturing processes. Great progress has been made in the area of global warming perfluorocompound (PFC) emissions: Technologies have been developed that can provide up to two orders of magnitude lower emissions from Etch and CVD chamber cleaning, compared to the processes of records of just a few years ago. Much can be learned from the strategy that was adopted to find solutions to the PFC problem. First, environmentally friendly technologies must conciliate process performance and economic viability. Second, one must realize that industrial processes are not developed in isolation from their surroundings but are rather part of an overall industrial ecosystem. This mind set is steadily gaining ground as business studies realize the gain in productivity that can be made by implementing green technologies. Here we review some methods and applications currently used in the semiconductor equipment industry to assess and reduce gas consumption and emissions, reduce solid waste and conserve energy and water resources.

3:20pm **AT-TuA5 Reducing PFC Emissions from a Semiconductor Wafer Fab: Optimization of Chamber Clean Processes for the CVD Tool Set*, A.D. Johnson,*** Air Products and Chemicals, Inc.*; C. Deuper,* Philips Semiconductor, The Netherlands

Perfluorocompound (PFC) gases (e.g., CF4, C2F6, and NF3) are used extensively in semiconductor manufacturing for cleaning CVD chambers following thin film deposition. PFCs, however, have large global warming potentials (GWPs) and are suspected of contributing to global climate change. Responding to this concern, the global semiconductor industry has voluntarily agreed to minimize its PFC emissions. Reduction targets for the

US, Europe and Japan are 10 % of 1995 levels by the year 2010. Achieving these targeted reductions requires all processes using PFCs be optimized. Process optimization involves reducing emissions, and usage, of PFCs while maintaining the same, or reducing, the cycle time. This report describes how optimized chamber clean processes were identified for the CVD tool set.

3:40pm **AT-TuA6 AMD's Global Climate Protection Plan***, **R. Content**,* AMD

Biomaterials
Room 102 - Session BI-TuA
Non Fouling Surfaces and Theoretical Concepts

Moderator: H.J. Griesser, CSIRO, Australia

2:00pm **BI-TuA1 Surface Forces and Coating Properties Involved in Protein Repellency***, P. Kingshott, H. Thissen, L. Meagher, P. Hamilton-Brown, **H.J. Griesser**,* CSIRO, Molecular Science, Australia **INVITED**

PEO coatings have attracted much interest as non-fouling coatings. However, literature data show varying extents of reduction in protein adsorption with PEO coatings prepared in various ways, and use of techniques that may not always have been sufficiently sensitive to support claims of non-fouling (as opposed to low-fouling). We have immobilized PEG chains of different lengths onto surfaces with different densities of pinning groups and at room temperature as well as under cloud point conditions to study how these parameters affects macromolecular conformations and protein resistance. We have also investigated the limits of detection of adsorbed proteins on the 'best' coatings by the sensitive surface analytical methos XPS, ToF-SSIMS and MALDI. Cell colonization was found to be totally inhibited and this could be attributed to the inability of fibronectin and vitronectin to adsorb to the coating. Using a laser ablation technique, patterns were then created of cell-adhesive islands within a PEO-coated surface area. It was shown that the cells recognized edges with high precision. Finally, surface force curves were acquired using a colloid-modified AFM tip in order to probe for the interfacial forces that contribute to incomplete or complete protein repellency. Our PEO coatings differ markedly in structure and some properties from oligo-EO coatings prepared by SAM methodology, yet give analogous results in terms of resistance to fouling. Based on this and data with polysaccharides (Hartley et al, this meeting) we speculate that protein resistance does not require a 'magic' chemistry or a fully extended 'brush' structure; a highly hydrated coating that possesses a repulsive surface force due to steric-entropic-osmotic effects on compression, of sufficient magnitude and range to screen attractive van der Waals and electrostatic forces emanating from the substrate, is sufficient. The chemical composition may not matter as long as the coating is well hydrated and of a minimal thickness, and protein repellency may solely be a result of appropriate physico-chemical properties. Moreover, charge neutrality is required, as negatively charged coatings such as hyaluronan are effective only against some fouling situations. For insance our PEO coatings are neutral and screen substrate charges, thus repelling proteins of both charge signs.

2:40pm **BI-TuA3 Water-Uptake of Poly(ethylene glycol)-terminated Self-Assembled Monolayers during Film Formation***, **J. Fick**, S. Tokumitsu, M. Himmelhaus, M. Grunze,* Universität Heidelberg, Germany

Self-assembled monolayers (SAMs) terminated by poly(ethylene glycol) (PEG; MW = 2000 Dalton) formed on polycrystalline gold have proven to provide an interesting model system for the study of grafted PEG chains with different morphologies, such as mushroom, polymer brush, and crystalline-like phase. The desired structure can be obtained simply by varying the immersion time of the substrate in solution, because the adsorbed molecules adopt the respective conformations as a function of coverage. As there is still a controversial discussion about the origin of the unique properties of PEG in terms of protein resistance and the roles that both, morphology of the PEG and bound water molecules might play, we have studied the water-uptake of the PEG-SAMs as a function of surface coverage by optical spectroscopies. The SAMs were adsorbed from solvent mixtures with distinct amounts of water added. We present the dependency of the adsorption kinetics as a function of various parameters, such as polarity, water-content of the solvent, and temperature during adsorption.

3:20pm **BI-TuA5 Novel PEO-containing Copolymers as Protein Repellent Additives In Polyurethanes: Evaluation of Protein Interactions by Radiolabelling, XPS and MALDI***, J.H. Tan,* McMaster University, Canada*; **K.M. McLean**, T.R. Gengenbach, H.J. Griesser,* CSIRO Molecular Science, Australia*; J.L. Brash,* McMaster University, Canada

Polyurethanes (PUs) have long been used for medical applications, mainly because of their excellent mechanical properties. However, there is a need to improve the biocompatibility of these materials. Polyethylene oxide (PEO) has gained recognition as a biocompatible material and appears to interact minimally with proteins and cells. In this work, materials have been developed based on PEO-containing additives that can be applied to conventional PUs. The additives are amphiphilic triblock copolymers, PEO-PU-PEO, the middle segment of which has the same structure as the PU substrate. We hypothesize that such additives should interact strongly and be compatible with any polyurethane of structure similar to the middle segment, and that they should migrate to the PU-aqueous interface. Copolymers were synthesized using PEO blocks of varying MW (550, 2000, 5000) and a central PU block of MW 5000. Materials were prepared by blending the block copolymers with a base PU. The surfaces were characterized by water contact angle and XPS. Adsorption of proteins was investigated by radiolabelling and by XPS. The water contact angle data showed that the blends became more hydrophilic with increasing copolymer content. Radiolabelled fibrinogen expts showed that adsorption was much lower on the blends than on the unmodified PU, in some cases showing reductions of greater than 99%. For the 10% blends, surprisingly, adsorption decreased in the order PEO5000>2000>550. This "inverse dependence" is attributed to slower diffusion of the higher MW copolymers to the interface. The protein adsorption characteristics were also investigated using XPS and surface-MALDI using a range of individual plasma proteins (fibronectin, vitronectin, albumin, insulin, fibrinogen and IgG) and whole plasma. XPS results confirmed that protein adsorption on the blends was negligible compared to the unmodified PU. Ongoing surface MALDI experiments also indicate low adsorption on the copolymer-PU blends.

3:40pm **BI-TuA6 Surface Modification of Poly(Vinyl Chloride) Intubation Tubes to Control Bacterial Adhesion***, **D.J. Balazs**, Y. Chevolot, K. Triandafillu, H. Harms, C. Hollenstein, H.J. Mathieu,* Swiss Federal Institute of Technology - Lausanne, Switzerland

Bacterial colonization of intubation tubes is responsible for 30% of all nosocomial pneumonia cases, 40 % of which lead to death, despite aggressive antibiotic therapy.@footnote1@ Therefore, a strategy to reduce bacterial adhesion is desirable. We are developing an approach based on the surface modification of the polymer used for this application, medical grade poly(vinyl chloride) (PVC). The strategy is to mask the PVC substrate with a chemically inert teflon-like fluoropolymer layer, which serves as an ideal platform for further surface modification due to its low surface energy.@footnote 2@ Protein@footnote 3@ and bacterial@footnote 4@ repellant molecules, e.g. amphiphilic Pluronics@super R@, are bound to the fluoropolymer films using hydrophobic-hydrophobic interactions. This paper investigates fluoropolymer films created on PVC substrates through plasma-enhanced chemical vapor deposition. The films are deposited in an RF-plasma reactor, using C@sub 2@F@sub 6@ as a precursor and H@sub 2@ as a carrier gas. XPS data suggest that the films completely mask the substrate, as no remaining signatures of PVC are detectable. Moreover, alpha step measurements show a uniform film, with a thickness of approx. 200 nm. The fluoropolymer films were found to be highly hydrophobic, with a water contact angle > 100 °. Preliminary contact angle measurements of the Pluronic@super R@ surfaces show a significant decrease in contact angle, (approx. 20 °) indicating adhesion to the fluoropolymer layer. Feedback from imaging XPS is then used to optimize Pluronic@super R@ monolayer formation on the fluoropolymer film. Protein adsorption and in vitro bacterial adhesion studies will also be reported. @FootnoteText@ @footnote 1@ J. L. Vincent et al (1995) JAMA 274: 639-644 @footnote 2@ I. Noh et al (1997) J Polym Sci Pol Chem 35: 1499-1514 @footnote 3@ M. Paulsson et al (1993) Biomaterials 14: 845-853 @footnote 4@ M. J. Bridgett et al (1992) Biomaterials 13: 411-416.

4:00pm **BI-TuA7 XPS-Mediated Robust Design Used to Optimize Hyaluronic Acid Surface Immobilization***, **T.A. Barber**,* University of California, Berkeley*; R.A. Stile,* Northwestern University*; D.G. Castner,* University of Washington*; K.E. Healy,* University of California, Berkeley, U.S.A

A major limitation of scaffold-based cartilage tissue engineering approaches is the inability of the delivery scaffolds to adhere to the tissue lining cartilaginous defects. Previously, thermo-responsive P(NIPAAm-co-

AAc) hydrogels were engineered to support chondrocyte viability and promote articular cartilage-like tissue formation in vitro. An objective of the current research is to functionalize these hydrogels with bioactive peptides to support specific interactions with components found in cartilaginous extracellular matrix (specifically Hyaluronic Acid (HA)). It is hypothesized that these interactions will significantly enhance scaffold-defect adhesion. A model HA surface was developed to test this hypothesis by quantifying these interactions. A commonly used strategy for HA surface immobilization exploits a carbodiimide reaction between the carboxylic acid groups present in HA, and an aminofunctional surface. However, a wide variety of reaction conditions have been reported, and it is unclear which elements are critical to this HA-grafting approach. Consequently, Robust Design methods were employed to optimize the HA-grafting procedure on aminofunctional glass substrates. First, a 4-factor, 3-level orthogonal array (L@sub9@) was constructed to monitor the effects of HA concentration, coupling buffer (CB), CB pH, and Carbodiimide/N-Hydroxysulfo-succinimide concentration ([EDC/NHS]) on HA-grafting success. XPS C/Si ratios were used to assess factor effects. Deconvolution of the L@sub9@ identified HA concentration, CB, and [EDC/NHS] as the dominant process variables. Subsequently, a 3-factor, 2-level orthogonal array (L@sub4@) was used to further refine the HA-grafting conditions. Evaluation of the L@sub4@ suggested optimal levels for HA concentration (2.5µM), CB (10mM HEPES), and [EDC/NHS] (100mM/25mM). Optimal grafting conditions will be utilized for preparing model surfaces to evaluate the adhesive properties of the functionalized gels using JKR adhesion testing.

5:00pm **BI-TuA10 Theoretical Prediction of the Enthalpic and Entropic Contributions of the Change in Gibbs Free Energy for Peptide Residue Adsorption onto Functionalized SAM Surfaces*, R.A. Latour,*** Clemson University

The thermodynamic energy contributions of the change in enthalpy (dH) and entropy (dS), and their summation to calculate the change in Gibbs free energy (dG), provide a very useful tool to predict complex biomolecular behavior. This approach has been successfully applied to address a wide range of biomolecular problems such as the prediction of protein and RNA folding and ligand-receptor binding for rational drug design. A similar approach holds great potential to be applied to understand and predict the adsorption behavior of proteins to synthetic surfaces. A protein is composed of specific sequences of peptide residues arranged in a well-defined structural organization. Protein-surface adsorption can be expressed as a set of intermolecular (residue-surface) and intramolecular (residue-residue) interactions with the minimization of these energetic contributions determining the final conformation and orientation of adsorbed protein. In this study, computation chemistry (MOPAC/PM3/COSMO) was combined with wetting data to predict dH, dS, and dG contributions for the adsorption of individual peptide residues (alanine, serine, lysine) on functionalized SAM surfaces (methyl, hydroxyl, carboxyl) as a function of surface separation distance (SSD). The results are in close agreement with other more generalized continuum-based theories of adsorption and predict how dH and dS from residue/surface and solvent restructuring effects contribute uniquely for each residue/surface pair. These results will serve as the foundational building blocks of more advanced treatments to quantitatively predict protein adsorption behavior with subsequent application for biomaterials surface design.

Dielectrics
Room 130 - Session DI-TuA
High K Dielectrics III

Moderator: S. Zollner, Motorola SPS, PMCL

2:00pm **DI-TuA1 Post-deposition Densification of Yttrium Oxide High Dielectric Constant Insulators Deposited by Oxygen Plasma Assisted Chemical Vapor Deposition*, D. Niu,*** *R.W. Ashcraft, G.N. Parsons,* North Carolina State University

Understanding and controlling interface and bulk chemical stability of CVD high-k dielectrics is an important research issue. Several groups report that the equivalent oxide thickness of vapor deposited dielectrics changes during post-deposition processing, but mechanisms that control the changes are not well understood. We examine the effect of post-deposition annealing on yttrium-based high-k dielectrics formed by oxygen plasma assisted CVD at temperatures between 350 and 450°C. Using yttrium-based materials, our group has previously demonstrated dielectrics with equivalent oxide thickness of 10-12Å with k=14. In this work, depositions were compared on Si(100) using two different yttrium diketonate precursors introduced downstream from a remote oxygen plasma source. Physical film thickness ranged from 1000Å, and films were characterized using IR, XPS and IV and CV electrical analysis, before and after annealing at temperatures >900°C. For the thin films, XPS indicates mixing of yttrium and oxygen with silicon at the substrate interface during deposition. Over a wide range of thickness, as deposited Y@sub2@O@sub3@ films show evidence for O-H and C-H bonds in the IR spectra. After annealing at 900°C in N@sub2@ (with >10@super-5@ Torr O@sub2@ pressure), the IR shows almost complete removal of O-H and C-H bonds. The films also show a remarkable decrease in macroscopic thickness (e.g. from 600Å to ~400Å after annealing at 900°C for 10 minutes), which cannot be accounted for simply by film crystallization. After anneal CV analysis shows good behavior, with evidence for positive fixed charge and substrate oxidation. This data suggests that density of as deposited CVD dielectrics is a critical issue, and hydroxyl bonds present in as-deposited films can react at the interface during post-deposition annealing. Approaches to control hydroxide incorporation and improve material stability will be presented and discussed.

2:40pm **DI-TuA3 Substitutional Effects of the Dielectric Constant in Ta@sub 2@O@sub 5@*, K. Larsson,*** *J. Westlinder, H.-O. Blom, J. Olsson,* Uppsala University, Sweden

Tantalum pentoxide (Ta@sub 2@O@sub 5@) is considered to be a promising candidate as a dielectric material. The reported dielectric constant (@epsilon@? for Ta@sub 2@O@sub 5@ ranges between 20-40. Depending on annealing temperature, process temperature and process method, the Ta@sub 2@O@sub 5@ films have crystallised into different phases. Since @epsilon@ is greatly dependent of phase of Ta@sub 2@O@sub 5@ as well as dependent of various solutions of additives (e.g., Ti, Zr, Nb), it is of a large interest to study and compare different phases and solutions separately. The purpose with the present study has been to theoretically investigate the substitutional effect of various additives (Ti, Zr, Hf, V, Nb, Sn) in the @beta@-phase of Ta@sub 2@O@sub 5@ on the dielectric constant. The ionic, as well as the electronic, part of the dielectric function have then been calculated for mono-crystalline materials, using the first principle Density Functional Theory. In addition, the electronic part of @epsilon@ has also been calculated for a polycrystalline material as well. In the present study, an atomic substitution of 12 % of Ta with Ti, Zr, Hf, V, Nb and Sn, respectively, has been performed with a maintained ideal stoichiometry. For the situation with a Ti solution, the substitutions of 8 and 13 atom% were also used. As a general result, dielectric constants very similar to experimentally obtained values have been theoretically calculated in the present investigation.

3:00pm **DI-TuA4 Ta d-state Derived Electron Traps in non-Crystalline Al@sub 2@O@sub 3@-Ta@sub 2@O@sub 5@ Alloys Prepared by Remote PECVD*, R.S. Johnson,*** *J.G. Hong, G. Lucovsky,* North Carolina State University

The bonding coordination of Al and Ta in Al@sub 2@O@sub 3@ and Ta@sub 2@O@sub 5@ is known, respectively, from Al27 nuclear magnetic resonance, NMR,@footnote 1@ and X-ray diffraction, XRD.@footnote 2@ There are 4- and 6-fold coordinated Al-atoms in non-crystalline Al@sub 2@O@sub 3@ and these are bonded to 3-fold coordinated O-atoms. XRD of high temperature crystalline Ta@sub 2@O@sub 6@ indicates a mix 6- and 8-fold coordinated Ta, with 2- and 3-fold coordinated O-atom neighbors. FTIR and Raman studies confirm similar bonding arrangements in non-crystalline Ta@sub 2@O@sub 5@. Non-crystalline Al@sub 2@O@sub 3@-Ta@sub 2@O@sub 5@alloys have been prepared by remote PECVD. Robertson@footnote 3@ has shown that the anti-bonding Ta d-state energy levels are significantly below the p-states of Al and Si and cause a reduced conduction band offset with Si of ~0.36 eV. Miyazaki@footnote 4@ has measured band offsets by photoemission and has found good agreement with theory. The temperature dependence of C-V and J-V traces for capacitors with Al@sub 2@O@sub 3@-Ta@sub 2@O@sub 5@ dielectrics indicate trapping and trap release that is consistent with the trapping states being associated with anti-bond d-states of Ta. In particular, hysteresis in the C-V traces is consistent with electron trapping, and is significantly increased by addition of Ta@sub 2@O@sub 5@ into Al@sub 2@O@sub 3@. The temperature dependence of J-V traces, combined with the C-V traces is consistent with different activation energies for electron trapping, and trap release. The energies obtained from analysis of the data are in agreement with conduction band offset energies determined from the photoemission studies of Miyazaki.@footnote 4@ The activation for electron injection into Ta trapping states is 0.30±0.05 eV, consistent with the energy of empty Ta-atom d-states relative to the Si conduction band. The activation energy for trap release is 1.5±0.1 eV, in agreement with the energy difference between these Ta d-states and the Al@sub 2@O@sub 3@ conduction band position as determined from band offset energy measurements.@footnote 4@ Supported by the Office of Naval Research and the SEMATECH/SRC Front End Processing Center @FootnoteText@ @footnote 1@ D. Muller, W. Gessner, H.J. Behrens, and G. Scheller, Chem. Phys. Lett. 59, 79 (1981). @footnote 2@ N.C. Stephenson and R.S. Roth, J. Solid State Chem. 3, 145 (1971). @footnote 3@ J. Robertson, J. Vac. Sci. Technol. B 18, 1785 (2000). @footnote 4@ S. Miyazaki, presented at PCSI 28, Lake Buena Vista, FL, 7-11 January 2001, submitted to J. Vac. Sci. Tech. B (2001).

3:20pm **DI-TuA5 Angle-Resolved XPS and Auger Analysis of Ultra-Thin Al@sub 2@O@sub 3@ Films Deposited by Atomic Layer Deposition***, **O. Renault**, D. Rouchon, L. Gosset, A. Ermolieff,* CEA/Grenoble-LETI, France

Ultra-thin (1-4.5 nm) aluminium oxide (Al@sub 2@O@sub 3@) films prepared by Atomic Layer Deposition on HF-passivated Si substrates were characterized by ARXPS and AES. Results were analysed in terms of chemical quality of the oxide layer as well as physico-chemical characteristics of the intermediate layer, before and after RTP annealing. For both as-deposited and annealed films, Al2p and Si2p line analysis revealed that only Al-O bonds were present (neither Al-Al bonds@footnote 1@ nor silicate-type compounds@footnote 2@ were observed at the interface with the substrate); the films, as well as 50 nm-thick ones, were found to be stoechiometric with O/Al ratios around 1.5. For as-deposited films, decomposition of the O1s line evidenced the formation of Al-OH groups@footnote 3@ during the deposition process; their concentration was maximum at the surface and decreased as the depth probed increased; this additional contribution of Al-OH bonds to the O1s signal was not observed on annealed films. Results gained from both decomposition of the Si2p line at different analysis angles and AES depth profiling showed that an intermediate layer of oxidized Si grows up upon annealing, its thickness being related to that of Al@sub 2@O@sub 3@ and equal to 0.6±0.2 nm for 2.5 nm-thick films; sub-oxides appear to be localized at the Si interface whereas fully oxidized Si forms above. Additional results concerning films deposited on thermally grown SiO2-coated Si substrates will be also presented. @FootnoteText@ @footnote 1@ Yang et al., Surf. Coat. Technol. 131 (2000) 79-83 @footnote 2@ Klein et al., Appl. Phys. Lett. 75 (25), 4001 (1999). @footnote 3@ Alexander et al., Surf. Interface Anal. 29, 468 (2000).

3:40pm **DI-TuA6 In-situ, Real Time Studies of Interface Formation of BST Thin Films on Si Substrates***, **A.H. Mueller**, N.A. Suvorova, E.A. Irene,* University of North Carolina, Chapel Hill*; O. Auciello,* Argonne National Laboratory*; J.A. Schultz,* Ionwerks, Inc.

The decrease in feature size of electronic devices and the commensurate electronic properties scaling has resulted in a search for new materials to achieve the electronic properties required for such miniature technologies. Ba@sub 0.5@Sr@sub 0.5@TiO@sub 3@ (BST) and other oxide films have become the front-runners in a search for materials to replace existing dielectrics in future technologies. Precluding the integration of BST as a gate dielectric into silicon devices are issues regarding the interface quality between the dielectric and semiconductor as well as the metal contact, as these affect critical electrical properties of the film such as the magnitude of the dielectric constant and the leakage current. In-situ studies of the oxygen incorporation into these films and the interface formation between BST films and Si substrates using time of flight ion scattering and recoil spectrometry (ToF-ISARS) as well as spectroscopic ellipsometry (SE) are presently being employed to ascertain conditions which minimize interface intermixing and maximize oxygen incorporation during reactive ion beam sputter deposition, and these studies comprise the focus of this presentation. Ex-situ material and electronic characterizations have also been used to characterize devices (Ir/ BST/ Si) prepared completely in vacuo and have shown the film's overall dielectric constant to be reduced by an intermixed layer of BST and Si substrate possessing an intermediate dielectric constant, while leakage characteristics of the film indicate a dependence upon the degree of oxygen deficiency as well as the BST/ metal contact interface quality. The electronic characterization studies will be presented separately.@footnote 1@ @FootnoteText@ @footnote 1@ N.A. Suvorova, A.H. Mueller, E.A. Irene, O. Auciello, and J.A. Schultz. Electrical properties of BST thin films on Si substrates. Present Conference Proceedings.

4:00pm **DI-TuA7 Direct Observation of Atomic Disordering at the SrTiO@sub 3@/Si Interface Due to Oxygen Diffusion***, **V. Shutthanandan**, S. Thevuthasan, Y. Liang,* Pacific Northwest National Laboratory*; Z. Yu, R. Droopad,* Motorola Labs

Since CMOS devices based on the conventional dielectric material, SiO@sub 2@, will soon reach their dimensional limits in device technology, alternative high dielectric materials received much attention in recent years. Several oxides are being considered as alternative dielectric materials and strontium titanate is one of the most attractive choices of such materials. Recently, single crystal SrTiO@sub 3@(100) films have been successfully grown on Si(100) substrates at Motorola.@footnote 1@ The stability of these films that were grown at Motorola was studied as a function of temperature under various control environments including vacuum, hydrogen and oxygen using Rutherford backscattering spectrometry (RBS) along with channeling techniques, nuclear reaction analysis (NRA) and x-ray photoelectron spectroscopy (XPS) at Pacific Northwest National Laboratory (PNNL).@footnote 2@ Results from channeling measurements are consistent with the reported thin silicate/silica layer at the interface of an as grown sample. Annealing experiments in the vacuum and hydrogen indicate more disordering at the interface and in the bulk of the film due to oxygen movement from the film to the interface for the growth of silica. On the other hand, annealing in oxygen show improvements in crystalline quality of both film and interface. Experiments with isotopic labeled oxygen (@super 18@O) were carried out to understand the oxygen diffusion through the film to the interface using @super 16@O and @super 18@O nuclear reactions. Film collapses in the temperature range of 1070-1120 K regardless of the heating environment. @FootnoteText@ @footnote 1@ Z. Yu, J. Ramdani, J.A. Curless, C.D. Overgaard, J.M. Finder, R. Droopad, K.W. Eisenbeiser, J.A. Hallmakrk, and W.J. Ooms, J. Vac. Sci. Technol. B 18, 2139 (2000). @footnote 2@ Work conducted at PNNL was supported by the DOE Laboratory Technology Research (LTR) Program and by Office of Biological and Environmental Research (OBER).

4:20pm **DI-TuA8 Core-level Photoemission of High-K Dielectrics on Si Substrates***, **J.E. Rowe**,* Army Research Office*; M.D. Ulrich, R.S. Johnson,* North Carolina State University*; T.E. Madey,* Rutgers University*; G. Lucovsky,* North Carolina State University

High resolution soft X-ray photoelectron spectroscopy (SXPS) with synchrotron radiation is used to study the interface of device quality ultrathin gate oxides of Al, Ta and Al-Ta alloys. Our present studies were performed on thin oxides grown plasma-enhanced CVD. After growth samples were further processed by rapid thermal annealing for 30 sec at temperatures near ~ 900ÂºC. Our photoemission measurements were performed with synchrotron radiation at the National Synchrotron Light Source (NSLS) located at Brookhaven National Laboratory using beamline U4A which has a total instrumental resolution of better than 0.1 eV. Some data were collected at lower resolution (~0.2 eV) in order to increase data collecting efficiency for better sampling depth at higher photon energies (near 200 eV). We find that our data can be well described by an ultrathin ~5 Ã… interface layer of SiO2 with a graded transition to Al and/or Ta oxides. We have studied a number of samples prepared as described above and find that the interface peak energies relative to the Si-2p peak are 0.81 eV, 1.75 eV, 2.47 eV, and 3.60 eV for the Si+1, Si+2, Si+3, and Si+4 peaks respectively. No evidence of sub-oxides were found for either Al or Ta species. The total concentration of Si-suboxide derived from SXPS data is dependent on the uniformity of the SiO2 interfacial layer as well as data modeling, i.e., fitting of the data; both will be discussed.

4:40pm **DI-TuA9 Quadrupole Mass Spectrometer Studies of a High Temperature Etch Process***, **St. Schneider**, H. Kohlstedt, R. Waser,* Forschungszentrum Juelich, Germany

High temperature etch processes are necessary to pattern Platinum successfully. In contrast to conventional, low temperature sputter driven etch processes, a chemical etch component is observed. >From the process perspective, they yield in redeposition free features (no fences) and in good control over sidewall sloping (minimization of CD loss). Furthermore those process regimes are characterized by a good process stability in terms of wafer counts and particle contamination, which is due to the dominating volatile etch products. To systematically investigate possible reactive etch process regions, we used a reactive ion etching (RIBE) tool with a filament free ICP source, that gives us control over the beam energy and the current density, and allows to use reactive gases. In this study we present the results for a chlorine chemistry with oxygen and carbonmonoxide additives. An energy dispersive quadrupole mass spectrometer is used for in-situ process monitoring. In one configuration, we are able to place the probe in the wafer position, opposite to the ion beam source. In this way it is possible to investigate the beam properties which are normally impinging on the wafer surface. In a second position we are able to lock on the wafer from the side, to monitor the etch process. Though the main focus of the study is on Platinum we also present results from selectivity studies to different hard mask materials and substrate materials.

5:00pm **DI-TuA10 Spectroscopic Ellipsometry Characterization of High-k Dielectric Thin Films*, N.V. Nguyen,*** *Y.J. Cho, R.A. Richter, J.R. Ehrstein,* National Institute of Standards and Technology

Spectroscopic ellipsometry (SE) characterization of high-k gate dielectric thin films will be presented in this paper. The materials investigated include HfO2, ZrO2, TiO2, and Ta2O5 films on silicon substrates. These films are candidates to replace traditional SiO2 gate dielectrics. Unlike SiO2, the dielectric functions for these high-k films are not yet established and are strongly dependent on deposition process and conditions. Therefore, the objective of this study is to assess and validate optical models that can reasonably represent the dielectric functions of these materials. The films used in this study were fabricated by different techniques including chemical vapor deposition, jet vapor deposition, and sputtering, and were post-deposition annealed at various high temperatures. To model the SE experimental data, single and multiple Tauc-Lorentz (TL) dispersion function(s) were employed for the dielectric functions of the films. It is found that a simple single TL can generally reproduce the dielectric function below and near the absorption edge. Above the edge, a summation of two or more TL dispersions is needed to improve data fitting. For samples annealed at high temperatures, additional new optical features due to structural changes in the films were seen in their dielectric functions, which require even more than two TL dispersions to fit the data. In addition, the effect of a possible oxide layer at the interface between the substrate and the films was examined in the relation with their determined dielectric functions. We also describe and evaluate the use of other optical dispersions such as harmonic oscillator approximations for high-k thin films and compare the results with those of TL dispersion. A brief discussion for using extended spectral range into vacuum ultraviolet region to characterize these and other high-k dielectric thin films will be presented.

Magnetic Interfaces and Nanostructures
Room 110 - Session MI+EL-TuA

Spintronics II: Spin Injection & Transport

Moderator: B.T. Jonker, Naval Research Laboratory

2:00pm **MI+EL-TuA1 III-V Based Epitaxial Magnetic Heterostructures: Large Tunneling Magneto-Resistance*, M. Tanaka,*** University of Tokyo, Japan **INVITED**

Tunneling magnetoresistance (TMR) is one of the most important phenomena for future spin-electronics devices. Here, we present very large TMR (>70%) in all-semiconductor magnetic tunnel junctions (MTJs), having (GaMn)As ferromagnetic electrodes separated by an ultrathin AlAs tunnel barrier.@footnote 1@ Trilayer heterostructures, (Ga@sub 1-x@Mn@sub x@)As(x=0.04, 50nm)/AlAs(d nm)/(Ga@sub 1-x@Mn@sub x@)As (x=0.033, 50nm), were grown on p@super +@GaAs substrates by low-temperature MBE. Mesa etched MTJs with the barrier thickness d ranging from 1.3nm to 3.0nm were fabricated, and showed clear TMR due to the change from parallel to anti-parallel magnetization of the two ferromagnetic (GaMn)As layers. Very high TMR ratios up to 75 % were observed at 8K for the junction with d=1.5nm. For d@>=@1.6nm, the TMR ratio was found to decrease with the barrier thickness. This behavior can be explained by calculations assuming that the wavevector k// of carriers is conserved in tunneling. This means that conventional Julliere's model is not valid in such epitaxial MTJs. Also, we have found that the TMR behavior strongly depends on the applied magnetic field direction, which is well explained by the cubic magneto-crystalline anisotropy of GaMnAs.@footnote 2@ Unlike the conventional MTJs made of polycrystalline ferromagnetic metals and an amorphous tunnel barrier, the present MTJs are all-epitaxial monocrystalline semiconductor-based junctions, which have the following advantages: (1) MTJs made of all-semiconductor heterostructures can be integrated with semiconductor circuitry. (2) Many parameters, such as the barrier height, barrier thickness, and Fermi energy of the electrodes, are controllable. (3) Introduction of quantum heterostructures, such as resonant tunneling structures, will be easier than any other material system. @FootnoteText@ @footnote 1@ Y. Higo and M. Tanaka, Physica E (2001), in press. @footnote 2@ Y. Higo and M. Tanaka, J. Appl. Phys. (2001), in press.

2:40pm **MI+EL-TuA3 Spin Filtering and Tunneling Magnetoresistance in Double Barrier Magnetic Heterostructures*, A.G. Petukhov,*** *D.O. Demchenko, A.N. Chantis,* South Dakota School of Mines and Technology

We report the results of our theoretical studies of spin-dependent resonant tunneling of holes in GaMnAs-based double-barrier magnetic heterostructures. Our approach is based on the k.p Hamiltonian with exchange-field parameters obtained from first-principle calculations and on multi-band transfer matrix technique. Zeeman splittings of the light hole (LH1) and heavy hole (HH2) resonant peaks are the most striking features of the calculated I-V characteristics of the structures with magnetic emitters. This finding is in good agreement with experimental data by H. Ohno et al.@footnote 1@ The splittings of other resonant channels are smeared due to various bandstructure effects. The resonant tunneling through magnetic quantum wells in GaAs/AlAs/GaMnAs/AlAs/GaAs resonant tunneling diodes displays even more pronounced Zeeman splittings of the resonant channels. These splittings strongly depend on the orientation of the magnetization. The spin polarization of the transmitted current is also quite significant and can be controlled by an external bias. This spin-filtering effect also leads to tremendous enhancement of tunneling magnetoresistance at small biases. @FootnoteText@ @footnote 1@H. Ohno et al., Appl. Phys. Lett. 73, 363 (1998).

3:00pm **MI+EL-TuA4 Magnetotransport in Digital Ferromagnetic Heterostructures*, T.C. Kreutz,*** *G. Zanelatto, R. Kawakami, E. Johnston-Halperin, E.G. Gwinn, A.C. Gossard, D.D. Awschalom,* University of California, Santa Barbara

Recent studies of digital ferromagnetic heterostructures (DFH), in which fractional monolayers (ML) of MnAs alternate with interlayers of low temperature (LT) GaAs, have shown that the Curie temperature, Tc, is sensitive to the separation between MnAs sheets.@footnote 1@ We report studies of in-plane magnetotransport in these structures, for Be-doped and nominally undoped LT GaAs interlayers with thicknesses from 10 to 40 ML. For undoped DFH grown at 260 C, structures with 10 ML interlayers show an anom alous Hall effect, while structures with 20 and 40 ML interlayers show only the ordinary Hall effect. The decrease in Tc with increasing interlayer thickness is accompanied by a decrease in the Hall carrier density and mobility. The magnetoresistance of the 10 ML sample has a similar field dependence to bulk GaMnAs. The 20 and 40 ML magnetoresistances are qualitatively different. Effects of Be doping are also considered for DFH samples.. @FootnoteText@ @footnote 1@ R.K. Kawakami, et al APL 2379 (2000).

3:20pm **MI+EL-TuA5 Theoretical Band Offsets in Magnetic Semiconductor Heterostructures: CdCr@sub 2@Se@sub 4@ on Si and GaAs*, J.M. Sullivan*,** *S.C. Erwin,* Naval Research Laboratory

Ferromagnetic semiconductors grown on semiconductor substrates are being widely investigated as spin injection sources for spintronics applications. Of the many issues critical to the injection efficiency, the band offset plays a central role. In particular, band offsets provide a direct link between microscopic parameters which can be determined theoretically, and macroscopic properties which can be measured experimentally. Moreover, magnetic band offsets can be tuned by methods well known from traditional band-offset engineering, and thus will be important for efforts to optimize injection efficiencies. Here we present first-principles results for the magnetic band offsets in heterostructures consisting of CdCr@sub 2@Se@sub 4@, an n-type ferromagnetic semiconductor with a Curie temperature of 130 K, grown on Si and GaAs substrates. We first use density-functional total-energy methods to explore and identify stable and metastable interface structures, taking into consideration different interface terminations, intermixing, and polar vs. non-polar interfaces. For the thermodynamically favorable interfaces we then apply standard first-principles methods@footnote 1@ for calculating the band offsets. Finally, we present detailed comparisons to recent experiments@footnote 2@ for these heterojunctions. @FootnoteText@ @footnote 1@ A. Franciosi and C. G. Van de Walle, Surf. Sci. Rep. 25, 1 (1996). @footnote 2@ D. Park et al., unpublished. .

3:40pm **MI+EL-TuA6 Effects of Interface Structure and Chemistry on Spin Injection Efficiency in Spin-LEDs, *R.M. Stroud*,** *Y.D. Park, A.T. Hanbicki, B.R. Bennet, B.T. Jonker,* Naval Research Laboratory*; G. Itskos, M. Furis, G. Kioseoglou, A. Petrou,* SUNY Buffalo

The efficiency of spin injection across a heterointerface can be strongly affected by the structure and chemistry of that interface. To quantify the relationship between interface quality and spin injection efficiency, spin-LEDs make an ideal test system. In a spin-LED, carriers with a net spin polarization are injected into a LED, where radiative recombination results in circularly polarized light emission. The optical circular polarization directly reflects the degree of the spin polarization of the injected current. By varying the growth conditions to vary the quality of the interface for ZnMnSe/AlGaAs/GaAs/AlGaAs spin-LEDs, injection efficiencies of 0 to 65% have been achieved. In this system, the primary structural defect, identified by cross sectional transmission electron microscopy, is a stacking fault that nucleates at the ZnMnSe/AlGaAs interface. Stacking fault densities ranged from 10@super 10@ cm@super -2@ for the lowest efficiency samples to < 10@super 8@ cm@super -2@ for the 65% efficiency sample., The optical polarization scales with the stacking fault density, which indicates that the spin injection efficiency is affected by the ZnMnSe/AlGaAs interface structure and chemistry. We compare results for growth on As- and Ga-terminated AlGaAs surfaces, and for structures grown with a Zn- and Se-initiated growth of the ZnMnSe polarized contact layer. These results demonstrate that although the spin injection efficiency is sensitive to interface quality, the spin injection effect is robust enough in all-semicondutor spin-LEDS to withstand moderately high defect densities, and can be produced using pre-grown LEDs. @FootnoteText@ @footnote 1@ This work supported by ONR and the DARPA SpinS program.

4:00pm **MI+EL-TuA7 Recent Developments in Spin Electronics***, A. Fert,* Université Paris-Sud, France **INVITED**

My talk reviews recent developments of the research in spin electronics at Unité Mixte de Physique in Orsay. I will focus on the three following topics: 1)Magnetization reversal by injection of a spin-polarized current: After an introduction on the effect predicted by Slonczewski (and also Berger), I will present experimental results obtained on pillar-shaped trilayers (collaboration with LPN-CNRS and University of Brest) and I will describe the pending problems in the understanding of the spin transfer mechanisms generating the reversal. Current-induced reversal could lead to general applications for the switching of spin electronic devices and I will present the perspective in this direction. 2)Magnetic tunnel junction (MTJ): Although applications of the magnetoresistance (TMR) of MTJ are already around the corner, physics of spin-polarized tunneling is still far from being clearly understood. I will present experimental results on epitaxial (single crystal) MTJ which shed light on the physical mechanisms of TMR. 3)Spin injection into semiconductors: the development of devices combining ferromagnets and semiconductors is an important challenge in spin electronics. I will present a model clearing up the conditions for efficient spin injection from a ferromagnetic metal into a semiconductor.

4:40pm **MI+EL-TuA9 Structural and Optical Characterization during Growth of Co on Ga@sub 1-x@In@sub x@As(001)***, **K. L@um u@dge**[1],* Technische Universität Berlin, Germany & University of Minnesota*; P. Vogt,* Technische Universität Berlin, Germany*; B.D. Schultz,* University of Minnesota*; C.J. Palmstrom,* University of Minnesota, United States*; W. Braun,* BESSY*; N. Esser, W. Richter,* Technische Universität Berlin, Germany

The growth of magnetic overlayers on semiconductors has received considerable interest due to their potential use in spintronic devices. The interface between the ferromagnet and semiconductor is critical to spin polarized transport across the interface. Thus, it is important to determine dependence of the interfacial structure and the crystalline quality of the ferromagnetic film on the substrate temperature and surface reconstruction. The initial growth of Co on GaAs(001) has been studied using STM, PES and reflectance anisotropy spectroscopy (RAS). The Co tends to be disordered when grown at room temperature. However, crystalline islands are observed at a substrate temperature of 430 K. STM-images taken during Co deposition show, that the substrate surface morphology does not change during deposition despite the change in surface reconstruction. The initial growth on the As-rich c(4x4) surface is different from the growth on the c(8x2) Ga-rich reconstruction. For growth on the c(8x2) surface two different growth modes can be distinguished. At first Co-atoms are adsorbed into rows to form one-dimensional chains. Further deposition results in epitaxial cubic islands. The PES data indicate two metallic components in the Ga3d core level. One is interpreted as resulting from CoxGay and the other from metallic Ga. The As3d core level contains two different components leading to the conclusion of As-Co bonds at the interface and access As on top. The influence of lattice mismatch on the structural and magnetic properties of the epitaxial Co-layer will be studied by Co growth on Ga@sub 1-x@In@sub x@As(001).

5:00pm **MI+EL-TuA10 Structural and Magnetic Characterization of the Fe@sub x@Co@sub 1-x@ / GaAs(100) Interface***, **B.D. Schultz**[2], L.C. Chen, A. Isakovic, J. Strand, P.A. Crowell,* University of Minnesota*; M.M.R. Evans,* University of Wisconsin-Eau Claire*; C.J. Palmstrom,* University of Minnesota

Two distinct surface contributions to the magnetic anisotropy can be used to control the magnetic properties of thin films of bcc Fe@sub x@Co@sub 1-x@ grown on GaAs (100). On bare GaAs (100), the sp@sup 3@ bonding in the zincblende structure results in a two-fold surface symmetry of the gallium and arsenic bonding and a (2x4)/c(2x8) surface reconstruction for an arsenic surface coverage ~0.75 monolayers. This two-fold surface symmetry reduces the expected cubic four-fold magnetic anisotropy for Fe@sub 1-x@Co@sub x@ films to a strong uniaxial magnetic anisotropy. However, four-fold symmetry is restored in films grown with an interlayer of Sc@sub 1-y@Er@sub y@As(100), in which the rock-salt structure provides an unreconstructed surface. Initial STM images of 0.10 monolayer deposited Fe@sub x@Co@sub 1-x@ on GaAs(100) (2x4)/c(2x8) surface grown by MBE at 95°C indicate isolated clusters of atomic dimensions with preferential attachment along the arsenic dimer rows. The images also indicate that the (2x4)/c(2x8) reconstruction remains relatively undisturbed by the initial nucleation and growth at this coverage. The deposition of bcc Fe@sub x@Co@sub 1-x@ on Sc@sub y@Er@sub 1-y@As(100) indicates there is no preferred nucleation site for the Fe@sub x@Co@sub 1-x@ atoms on the unreconstructed surface. Control of the interfacial properties of ferromagnetic metals and semiconductors is important for optimizing spin dependent transport across these interfaces. Spin dependent ejection of photo generated carriers from GaAs(100) into Fe@sub x@Co@sub 1-x@ ferromagnetic metal contacts has recently been observed. This paper will emphasize the correlation between the structure and chemistry of the Fe@sub x@Co@sub 1-x@/GaAs and Fe@sub x@Co@sub 1-x@/Sc@sub 1-x@Er@sub x@As/GaAs interfaces, determined by STM, RHEED, LEED, XPS, RBS, XRD and TEM, and the magnetic and transport properties. Supported by: ONR-N/N00014-1-0233, DARPA N/N00014-99-1-1005, and NSF-MRSEC NSF/DMR-9809364.

Manufacturing Science and Technology
Room 131 - Session MS-TuA

In Line and In Situ Process Control

Moderator: E.G. Seebauer, University of Illinois, Urbana-Champaign

2:00pm **MS-TuA1 Plasma Etch Endpoint and Diagnostic Fault Detection Using Evolving Window Factor Analysis***, **H.M. Anderson**,* University of New Mexico*; S. Gunther, B. Fry,* CETAC Technologies

Array detector based systems with statistical analysis capability integrated with real-time data acquisition can provide a wealth of spectral information from a variety of potentially useful gas phase emitting species. In the case of particularly challenging applications such as low-open area self-aligned contact (SAC) etches, utilization of the full optical emission spectrum has been shown to accurately detect endpoint when all other endpoint systems studied failed. Production facility results regarding these and other demanding applications will be presented. The talk will largely focus on oxide etching in AMAT MXP and TEL DRM platforms. Evolving Window Factor Analysis (EWFA) is the principal multivariate techniques used in the analysis. They allow one to dynamically track the principal components of the oxide etch process. EWFA is also shown to useful for automatic fault detection.

2:20pm **MS-TuA2 Characterization of Pattern Transfer from Litho to Etch Using Scatterometry***, **T.G. Dziura**, U. Whitney, A. Levy,* KLA-Tencor*; G.P. Kota, G. Peng, R.A. Gottscho,* Lam Research

Gate pattern transfer from the lithography after-develop-inspect (ADI) step to post-gate-etch clean was characterized with spectroscopic CD (SCD) measurements on a KLA-Tencor F5-SCD metrology platform. Data were collected on resist-BARC-a-Si gate-gate oxide-Si grating structures at ADI, post-BARC-etch, post-gate-etch, and after-clean-inspect (ACI). Three different gate etch processes were applied using a Lam Research TCP@super ®@ 9400DFM etcher to produce varying sidewall profiles. Measurements were made on grating targets with nominal CD ranging from 75 - 160 nm, and line/space ratios 1:1, 1:3, and 1:5. Both wafer map data and dynamic short-term repeatability data were collected. The profiles obtained were compared to cross-sectional SEM (XSEM) measurements. The CD bias between litho, BARC etch, and gate etch was measured for different nominal CDs and line-to-space ratios. The results

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[1] **Falicov Student Award Finalist**

[2] **Falicov Student Award Finalist**

indicate that SCD provides enhanced information for optimizing etch processes. Wafer maps of profile parameters can be measured at different stages of the process and correlation coefficients calculated between selected pairs of parameters provide insight into the pattern transfer process. The significantly increased resolution of SCD measurements enables more accurate and detailed process models.

2:40pm **MS-TuA3 Chamber Wall Monitoring and Control for Plasma Etching Reproducibility***, S.J. Ullal, T.-W. Kim,* University of California, Santa Barbara*; H. Singh, J. Daugherty, V. Vahedi,* Lam Research Corporation*; **E.S. Aydil**,* University of California, Santa Barbara

Wafer-to-wafer process reproducibility is one of the major concerns in plasma etching of thin films. Production of a uniform plasma with the same ion density, electron temperature, and species concentrations wafer after wafer is a major challenge. The plasma chamber walls play a crucial role in determining these discharge properties and remain as one of the major sources of irreproducibility. The problem of process sensitivity to the wall conditions has been known for a long time but its management has remained an art. Thus, it is critical to monitor the wall conditions and the nature of the films and adsorbates that are deposited on the walls. Towards this end, we have developed a surface probe based on in situ multiple total internal reflection Fourier transform infrared (MTIR-FTIR) spectroscopy that can be used as a diagnostic to monitor the films and adsorbates on the walls of both plasma etching and deposition reactors. This surface probe was used to study the nature of the species present on the walls of the chamber and process repeatability during Cl@sub 2@/O@sub 2@ plasma etching of Si. This etching process is particularly challenging because SiCl@sub x@ etching products react with O atoms to deposit a SiO@sub x@ Cl@sub y@ film on the chamber walls, which must be cleaned with an SF@sub 6@ plasma to ensure reproducible wall conditions. Infrared spectra of the films depositing on the walls were collected in real time during Cl@sub 2@/O@sub 2@ plasma etching of Si and during the SF@sub 6@ cleaning steps to determine and monitor the effect of each process step and the reproducibility of cleaning. The surface probe was used to minimize the duration of the cleaning step to maximize throughput and to develop cleaning strategies to improve wafer-to-wafer repeatability. Subtle drifts in etch profile shapes could be detected through the use of the MTIR-FTIR probe even though these drifts are not detected through etch rate measurements and other monitoring methods.

3:00pm **MS-TuA4 Integrated RF Sensor for Accurate Control and Monitoring of on Wafer Process Performance***, **A.M. Paterson**, J.M. McChesney, V. Todorov,* Applied Materials*; J. Holland,* Applied Materials, US*; M.S. Barnes,* Applied Materials

As the semiconductor industry moves to 300mm wafer size, it has become essential to have accurate and reliable knowledge of the RF and DC parameters experienced by the wafer being processed. Use of a RF sensor integrated on to the tool will provide accurate information useful for process optimization and repeatability analysis, however, correct placement of the sensor in the RF circuit is essential. Placement of the sensor directly in the wafer pedestal can make the design complicated, more expensive, and less accessible. This paper describes a more reliable method for obtaining the absolute RF and DC parameters on the wafer. This method utilizes accurate knowledge of the complete cathode impedance and an accurate circuit model describing the observed impedance. Accurate knowledge of the cathode impedance allows the RF sensor to be remotely placed, in our case in the RF match box, so that complicated cathodes designs can be avoided. Extensive work has shown that knowing the RF parameters at the output of the match, and the impedance of the cathode, that the RF and DC parameters calculated at the wafer are in excellent agreement with those values actually measured on the wafer. This method then allows for accurate chamber matching, endpoint and process control. Voltage compensation of the electrostatic chuck voltage in order to offset the effects of DC bias is also determined from this integrated probe. Other features of the RF sensor will also be discussed.

3:20pm **MS-TuA5 Fault Identification and Classification using a Plasma Impedance Monitor***, **M.P. Hopkins**, K. O'Leary,* Scientific Systems, Ireland **INVITED**

Semiconductor production fabs regularly encounter faults which result in unscheduled tool downtime. Among these are real-time tool faults, preventative maintenance recovery problems and tool mis-matching at start-up and process transfer. This downtime can be reduced by applying a Fault Detection and Classification scheme where the core problem is identified as rapidly as possible, replacing the usual "trial-and-error" approach to fault identification. Scientific Systems have developed a non-intrusive, high-resolution impedance sensor which is designed to aid fault identification. The sensor is used to characterize a baseline process, operating within control limits, by measuring the Fourier components of RF voltage, current and phase. This results in a unique impedance fingerprint of the chamber. When a fault condition occurs, the impedance fingerprint varies in a predictable pattern. By comparing the fault fingerprint to the baseline, it is possible to classify faults through a diagnostic methodology. Using the system, hardware problems can be separated from process issues and changes in individual process inputs can be identified. We report a number of case studies where the system has been successfully deployed.

4:00pm **MS-TuA7 Real-Time CVD Wafer State Metrology using a Downstream Acoustic Sensor***, **L. Henn-Lecordier**,* University of Maryland, US*; J.N. Kidder, G.W. Rubloff,* University of Maryland*; A. Wajid, C.A. Gogol,* Inficon, Inc.

An acoustic gas sensor, the Inficon Composer@super TM@, was implemented downstream in a production-scale tungsten chemical vapor deposition (CVD) cluster tool for process sensing to achieve real-time, in-situ film thickness measurements. Process gases were sampled at the reactor outlet and compressed with a diaphragm pump from the 10 Torr process pressure regime to above 50 Torr as required for gas sound velocity measurements in the acoustic cavity. Processes were carried out for various deposition times at 10 Torr, with a H@sub 2@ / WF@sub 6@ flow ratio of 6 to 1 and at wafer temperatures ranging from 300 to 450 °C. The sensor measures the average molecular weight of the gas mixture and is normally employed for control of inlet (upstream) gas flows into the reactor. For downstream applications, depletion of the H@sub 2@ and WF@sub 6@ reactants, as well as generation of the HF product, shift the gas composition with changes in reaction rate in the process. The high depletion rate of the WF@sub 6@ precursor (i.e. 30% or more) during blanket W deposition induced a substantial variation of the average molecular weight of the exhaust gas mixture. By integrating the resonant frequency over the deposition time, real-time in-situ metrology signals were obtained which correlated to post-process thickness measurements within 1%. This makes the acoustic sensor attractive for advanced process control, either in run-to-run control or through real-time end point control.

4:20pm **MS-TuA8 Thickness Metrology and Real-Time End Point Control in W CVD using in-situ Mass Spectrometry@footnote 1@***, Y. Xu,* University of Maryland*; L. Henn-Lecordier,* University of Maryland, US*; T. Gougousi, G.W. Rubloff, **S. Cho**, Y. Liu,* University of Maryland

In-situ downstream mass spectrometry has been employed in W CVD processes for real-time reaction sensing, thickness metrology, and real-time end-point process control. In the silane reduction process for depositing W CVD from SiH@sub 4@ + WF@sub 6@ using an Ulvac ERA-1000 cluster tool, high reactant reactant conversion rates were obtained at 200-250°C. Both depletion of the SiH@sub 4@ reactant and generation of the H@sub 2@ and SiF@sub 4@ reaction products provided real-time thickness metrology signals which correlated with post-process, ex-situ film thickness measurements with an uncertainty better than 2%. These metrology signals were used as end-points to terminate the process in real-time, leading to corresponding control of the mass spectrometry derived signal even in the presence of random run-to-run process fluctuations and systematic drift intentionally introduced as a run-to-run temperature drift. Actual film thicknesses as measured post-process were controlled to within 3% using this mass-spec-based end-point control. These results demonstrate that downstream mass spectrometry provides real-time thickness metrology suitable for real-time as well as run-to-run process control. Furthermore, the real-time end pointing capability enables compensation for random process fluctuations as well as systematic process drift. @FootnoteText@ @footnote 1@Present affiliations: Y. Xu (IBM Microelectronics, Hopewell Junction, NY); T. Gougousi (North Carolina State University, Raleigh, NC).

4:40pm **MS-TuA9 In-situ FTIR Spectroscopy for Metrology of a Tungsten CVD Process***, **A. Singhal**,* University of Maryland*; L. Henn-Lecordier,* University of Maryland, US*; J.N. Kidder,* University of Maryland*; C.A. Gogol, J.F. Kushneir,* Inficon, Inc.

A Fourier Transform Infrared Spectrometer has been employed for downstream detection of reactants and reaction products in a tungsten chemical vapor deposition process. The objective of this work was to monitor reactant and product concentrations for metrology of the deposition rate on the wafer. The spectroscopy system includes a novel compact interferometer and a heated optical cell with purged optics.

Measurements of the gas composition directly downstream of the wafer were done using a pumped sampling system to extract gases from the low pressure CVD process to the optical cell. Experiments showed a linear correlation between the gas concentration in the deposition chamber and the intensity of absorption features detected at the sampling optical cell. In experiments with repeated wafer load/unload and process flow sequences there was no significant drift in the detected steady-state intensity of absorption peaks. In measurements done during deposition process runs at a range of conditions the intensity of absorption features associated with a reactant (WF@sub 6@) and a principal reaction product (HF) were detected and correlated to the weight gain on the wafer for in-situ metrology of the deposition rate.

5:00pm **MS-TuA10 New Mass Spectrometer without Fragment Ions for CVD In-situ Monitoring***, **Y. Shiokawa**, M. Nakamura, K. Hino, T. Sasaki,* Anelva Corporation, Japan

In-situ gas monitoring of CVD depending on complicated reactions is more essential and has three objects; residual gases, materials and byproducts (precursors). Residual gases can be measured but the others are difficult by a conventional mass spectrometer using electron impact (EI) ionization. The reason is fragmentation; molecules with low binding energy for CVD are inevitably dissociated and become fragment ions. Therefore, we have developed a new apparatus as commercial product by means of Ion Attachment Mass Spectrometry (IAMS),@footnote 1@ in which a metal ion attaches to a molecule and the excess energy is so small that fragmentation could be avoided. First, we measured PFCs gases exhausted from a plasma-etching system.@footnote 2@ The mass spectra by IAMS showed every natural molecular ion corresponding to materials and byproducts, while not molecular ions at all but merely many fragment ions by EI. So, some diagnostics as well as monitoring was done. Next, we have applied to CVD. Some parts about gas introduction and metal ion emission have been improved because CVD gases are more adsorptive and adhesive. The apparatus, connected to the process chamber of Plasma-CVD, measured SiH@sub 4@, NF@sub 3@ and others as molecular ions. On the other hand, although a metallic-organic molecule for Cu deposition by MO-CVD has very low binding energy, its molecular ion was successfully detected. In-situ monitoring of MO-CVD using low vapor pressure materials is especially desired and seems to be realized by IAMS. We would like to present some examples of CVD in-situ monitoring throughout our talk. @FootnoteText@ @footnote 1@ T.Fujii, Mass Spectrometry Review 19 (2000) 111 @footnote2@ M.Nakamura et al JVST-A Vol.19,No4 (2001) to be published

Nanometer Structures
Room 133 - Session NS-TuA
Novel Surface Nanoprobes

Moderator: M. Tsukada, University of Tokyo, Japan

2:00pm **NS-TuA1 Nano-scale Science by Means of UHV Electron Microscopy***, **K. Takayanagi**[1],* Tokyo Institute of Technology, Japan **INVITED**

Nano-scale materials attract interest in fundamental science and technology. Because nano-meter scale materials behave as a new matter, differently from the condenced matter or liquid. As seen from magic number of clusters and carbon nanotubes, nano-scale matter presents degitized and/or quatized characteristics. These characteristics relate with nature of their surface characteristics. We developed an UHV high-resolution electron microscope combined with a miniaturized STM , which enabled us to study nanowires extending our previous analysis on Si(111)7x7 reconstruction. The gold nanowires were found to have multi-tube structure, like carbon nanotubes. In gold tube, each tube consits of gold atomic rows which coil the axis of the tube. The number of atomic rows in the outer tube increases by seven from that of the inner tube, so that the shell closing number is seven. The present STM combined UHV-TEM allow us to open new sciece of the nano-scale matter.

2:40pm **NS-TuA3 Tunneling Spectroscopy of Superconducting Quasiparticles by Scanning Tunneling Microscope with a Bulk NbN Tip***, **H. Bando**, Y. Aiura, K. Mitsugi,* National Institute of Advanced Industrial Science and Technology, Japan*; K. Oguchi, Y. Nishihara,* Ibaraki University, Japan*; Y. Kumashiro,* Yokohama National University, Japan

Use of superconducting tip is expected to extend the capability of scanning tunneling microsopy by allowing detection of superconducting quasiparticles in the atomic resolution. A few groups have succeeded in the measurements with supercunducting tips made of Nb or Ag/Pb coated PtIr, however, technically there remain challenges as for the cleaning of tip apex etc. We employed bulk NbN crystals, whose surface is chemically stable, and prepared tips by fracuture. Results of topographic measurements, SIN tunneling on Au, and SIS' tunneling on NbN films with the tunneling resistance varied for orders of magnitute are presented.

3:00pm **NS-TuA4 Demonstration of a Tunable Bistable Tunnel Device with a Low Temperature STM and a Self-organized Ga Array on Si(111)@footnote 1@***, **I.B. Altfeder**,* Harvard University*; D. Chen,* Rowland Institute for Science

Self-organized nano-structures on Si substrates have drawn much current research effort. The usefulness of these structures critically depends on physical properties they can offer for potential nanoscale device applications. We report here an unusual bistable transport behavior of a tunnel junction form between an STM tip and a two dimensional (2D) Ga array self-assembled on a Si(111) substrate. At 77K, large hysteresis loops appear in the I-V spectra when electrons are injected from the tip to the 2D Ga array, characteristic of the switching between ON - OFF conductance states. The turn-on bias varies from -3.1 V to -4.0 V and shows an inverse dependence on the tip-sample distance, indicating a strong field effect. The turn-off bias, however, is essentially pinned at a conductance threshold of -2.7 V. These observations demonstrate the basis of a nanoscale tunable bistable tunnel device with the potential for digital and storage applications. @FootnoteText@ @footnote 1@I. B. Altfeder and D. M. Chen, Phys. Rev. Lett. 84, 1284 (2000).

3:20pm **NS-TuA5 Theory and Perspective of the Spin-Polarized STM***, **S. Blügel**,* Forschungszentrum Jülich, Germany **INVITED**

In the frontier field of nano-magnetism understanding complex magnetic structures is crucial. We demonstrate that the spin-polarized scanning tunneling microscope (SP-STM) offers a great potential to unravel complex magnetic superstructures on different length scales. Different operating modes of a SP-STM@footnote 1@ will be discussed: It is shown that the spectroscopy mode (SP-STS) and the modulating tip-magnetization mode (SP-STMTM) are ideal to analyze complex magnetic structures on a mesoscopic length scale as created by atomic-scale ferromagnetism. Further we propose the application of the constant-current mode of a SP-STM for the investigation of surfaces of complex atomic-scale magnetic structures of otherwise chemically equivalent atoms. A recent application@footnote 2@ gave evidence of the capabilities of the SP-STM in terms of the first unambigious proof of two-dimensional antiferromagnetism in magnetic monolayer films on non-magnetic substrates predicted already in 1988.@footnote 3@ We argue, that in general any magnetic superstructure leads to an SP-STM image characteristic of the superstructure and is not superimposed on the image of the chemical lattice. This opens the door to study even more complex magnetic structures such as non-collinear spin-structures or spin-density waves. We present calculated SP-STM images of frustrated antiferromagnets on triangular lattices: a coplanar non-collinear periodic Néel state for Cr/Ag(111) and a multiple spin-density wave state of a Mn-monolayer on Cu(111), which we determined in Ref.@footnote 4@ to be the magnetic ground states of these systems. All calculations are based on the vector-spindensity formulation of the density functional theory. @FootnoteText@ @footnote 1@ D. Wortmann et al., Phys. Rev. Lett. 86, accepted (2001). @footnote 2@ S. Heinze et al., Science 288, 1805 (2000). @footnote 3@ S. Blügel et al., Phys. Rev. Lett. 60, 1077 (1988). @footnote 4@ Ph. Kurz et al., Phys. Rev. Lett. 86, 1106 (2001).

4:00pm **NS-TuA7 Charge Imaging of Electrons and Holes Trapped in Gate Oxides and at the Oxide-silicon Interface***, **R. Ludeke**, E. Cartier,* IBM T.J. Watson Research Center

We have observed individual electrons and positive charge both in bulk SiO@sub 2@ and Al@sub 2@O@sub 3@ gate oxides, and trapped on dangling-bond derived states (P@sub b@ centers) at the SiO@sub 2@-Si(111) interface. The charge is observed as sharp virtual holes in the surface topography measured with an Atomic Force Microscope operating in the non-contact mode in ultra high vacuum (UHV). The polarity of the charge was ascertained from contrast differences in Kelvin images that were simultaneously acquired with the topographs. The trapped charges in the bulk of the oxides exhibited a tendency to cluster. The P@sub b@ centers were created by the removal of H from the H-Si interfacial bonds by annealing the Si(111) samples to 600°C. Their densities in the mid 10@super 12@ cm@super -2@ range were measured with the AFM and confirmed by capacitance-voltage experiments. The distributions of the

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[1] **IUVSTA Award Winner**

negatively and positively charged (holes) traps are peaked, respectively, in the upper and lower halves of the band gap. This allows the selective capture of electrons or holes that depends on the position of the local Fermi level E@sub F@. E@sub F@ is controlled by the bias applied to the metallic AFM tip. We have modeled the band bending beneath the tip, which, depending on the bias and the binding energy of the trap state, can lead to temporary filling of the trap that leads to unusually sharp features in the images. Thus the trap's physical location and, less directly, the trap level relative to the band edges can be ascertained from these experiments.

4:20pm **NS-TuA8 'Artifact-free' Electrostatic Force Measurement using Noncontact Atomic Force Microscopy***, **K. Okamoto**, Y. Sugawara, S. Morita,* Osaka University, Japan

Noncontact atomic force microscopes (NC-AFM) using frequency modulation (FM) method have the potential ability to obtain surface structure of any materials, such as metals, semiconductors and insulators with atomic resolution. NC-AFMs simultaneously detect several kinds of forces acting between the tip and the sample surface; the van der Waals force, the chemical bonding force and the electrostatic force (ESF) et al. Each of the forces contains the different physical information about the surface. Although each of them is desirable to be separately detected, no method to completely separate them has not been realized. This lack results in the deviation of the NC-AFM images, namely the 'artifacts.' In this presentation, we propose the novel method to completely separate the ESF from other forces. The Kelvin probe force microscopy (KPFM) is often used to measure and separate the ESF with AFM. However, the KPFMs still involve an extra deviation, which is due to an AC electric field applied for KPFM measurement. Our new method proposed here can completely eliminate the influences due to the ESF on the topography with keeping all merits of KPFM by introducing the artifact eliminator circuit, which adjust the signal for height regulation of the tip. Our method can measure the topography and the spatial distribution of the ESF, which reflects the spatial distribution of work function or charges on the sample surface, with the atomic resolution without the 'artifact.' This system has high possibility to identify the kind of each atom.

5:00pm **NS-TuA10 Scanning Impedance Microscopy: From Impedance Spectra to Impedance Images***, **S.V. Kalinin**, D.A. Bonnell,* University of Pennsylvania

Electrostatic force sensitive scanning probe microscopy (SPM) for quantitative imaging of dc and ac transport behavior of electrically active interfaces is presented. SPM is used to study transport properties of a metal-semiconductor junction and SrTiO@sub 3@ bicrystal grain boundary. Scanning Surface Potential Microscopy (SSPM) of laterally biased sample is used to quantify potential drops at the interface. Varying the lateral bias allows the voltage and I-V characteristics of the interface to be reconstructed. A novel scanning probe technique based on phase change of cantilever oscillations induced by a lateral bias applied to the sample is presented. This technique, further referred to as Scanning Impedance Microscopy (SIM), allows mapping of the local voltage phase angle and voltage oscillation amplitude in complex systems. The frequency dependence of the voltage phase angle shift across the interface allows interface capacitance and resistance to be determined locally. Quantitative agreement between metal-semiconductor junction capacitance obtained from SIM measurements and macroscopic impedance spectroscopy is demonstrated. Variation of the dc component of lateral bias in SIM allows reconstruction of the C-V characteristics of the junction. SSPM and SIM imaging of a SrTiO3 grain boundary has demonstrated the non-linear transport properties of the interface and identified a large density of interface states at the boundary. The combination of SSPM and SIM provides an approach for the quantitative analysis of local dc and ac transport properties from SPM data and provides spatially resolved impedance spectra of complex microstructures. Finally, the applicability of SIM to characterize complex polycrystalline materials will be demonstrated.

Plasma Science
Room 103 - Session PS1-TuA

Dielectric Etch I

Moderator: M.J. Kushner, University of Illinois, Urbana

2:00pm **PS1-TuA1 Gas Phase and Surface Diagnostic Measurements of High-density Plasma-based Etching Processes for Dielectrics Based on C@sub 4@F@sub 8@ Gas Mixtures with Ar, O@sub 2@ and N@sub 2@***, **X. Li**,* University of Maryland*; M. Fukasawa,* Sony Corporation, Japan*; G.S. Oehrlein,* University of Maryland*; M. Barela,* University of New Mexico, U.S.*; H.M. Anderson,* University of New Mexico

High-density plasma etching of dielectric films, e.g. SiO2 and low dielectric constant films, is an important process steps in integrated circuit manufacturing. Etching selectivity relative to the etching mask and insulating etch stop materials is required for these processes. Frequently gas mixtures rather than pure fluorocarbon gases are being employed. In this work we have studied the effect of adding O2 and Ar, two important gas additives, to C4F8 discharges produced using an inductively coupled plasma source. We measured fluorocarbon deposition and etching rates, SiO2, resist and silicon etching rates as a function of gas composition. In parallel, the absolute partial pressures of CF2, CF and COF2 radicals were measured using infrared laser absorption spectroscopy. Mass spectrometry was used to establish the importance of other gas phase species. In-situ ellipsometry and x-ray photoemission spectroscopy were used to obtain information on the surface processes for the various thin film materials. The effect of admixing O2 or Ar is shown to produce dramatic and non-obvious changes in the gas phase and surface chemistry, and enables to better address the technological objectives of the etching process. For instance, we have observed that the SiO2/resist and SiO2/Si etching selectivity can be increased by more than a factor of 3x at 20 mTorr by adding about 50% of Ar to C4F8. The infrared absorption measurements show that the partial pressures of CF and CF2 are increased by the addition of Ar despite the lower partial pressure of C4F8, and thicker fluorocarbon surface reaction layers are produced on silicon surfaces during steady-state etching.

2:40pm **PS1-TuA3 A 0.09µm-capable Plasma Etching of Dielectrics and its Reaction Mechanism***, S. Tachi,* Hitachi, Ltd., Japan*; **J. Ghormley**,* Hitachi America Ltd. **INVITED**

For a well-controlled dielectric etching with 0.18-0.13µm capability, a considerable amount of molecular species, CF@sub 2@, has been needed in conjunction with an intentionally suppressed fluorine, F, in (C@sub 4@F@sub 8@/C@sub x@F@sub y@+Ar) plasma, and, at the same time, having a sufficient ion-flux. Multi-dissociative collision phenomenon and multiple gas fragmentation should be avoided in gas phase for this purpose. For designing such plasma, chamber geometry, and processes, further evolution seems to be necessary. In this paper, a highly selective contact etching against the photo-resist mask over the whole wafer, and a relatively high oxide etch rate with good reproducibility are discussed in terms of a new planer-type, high-medium density plasma, having a doubled-near-surface structure, and experimenting with a noble processing with a computationally feed-forwarded architecture.

3:20pm **PS1-TuA5 Plasma Etching Chemistry and Kinetics for Silicon Oxide Thin Films***, **O. Kwon**, H.H. Sawin,* Massachusetts Institute of Technology

Surface kinetics study of silicon oxide etching with fluorocarbons in inductively coupled plasmas High density fluorocarbon plasma for silicon oxide etching has various ion and neutral species. Depending on the plasma condition, many difficulties arise such as RIE lag, etch stop, and low selectivity of photoresit. Profile evolution modeling can provide understanding of these difficulties in etching as well as trenching, bowing, and faceting. In this research we have measured etching and deposition rates as functions of ion bombardment energy, ion impinging angle, ion-to-neutral flux ration, which are necessary for profile evolution modeling of silicon oxide etching in inductively coupled plasma. In this work, ions and neutrals are extracted directly from plasma to differentially pumped side chambers. Surface reaction is studied by measuring etching and deposition rate with quartz crystal microbalance(QCM). At the same time, ion and neutral composition of the plasma is determined with mass spectrometer. Etching or deposition rate is measured with QCM as functions of ion acceleration energy, ion impinging angle, ion-to-neutral flux ration with various fluorocarbon plasmas. With florocarbon plasma with deposition chemistry, fluorocarbon deposition was observed at low ion energy, high ion impinging angle, low plasma power and high pressure. A model describing both deposition and etching regimes is suggested.

3:40pm **PS1-TuA6 Oxide Etch Behavior in an Inductively Coupled C@sub 4@F@sub 8@ Discharge Characterized by Diode Laser Spectroscopy***, H.M. Anderson,* University of New Mexico*; M. Barela,* University of New Mexico, U.S.*; **G. Courtin,*** University of New Mexico*; K.S. Waters,* Intel

An inductively coupled GEC Reference Cell has been modified to allow etching of oxide wafers under conditions typical of commercial high density plasma reactors. This study reports on the oxide and photoresist etch characteristics as a function of reactor source power, bias power and pressure. Diode laser absorption spectroscopy (DLAS), OES and Langmuir probe measurements were made at the same time. DLAS has shown that C@sub 4@F@sub 8@ is largely dissociated to form C@sub 2@F@sub 4@, CF@sub 2@ and CF in the discharge. Over an oxide surface, CF@sub 2@ and CF are consumed in the oxide etch process, but only when the bias power is sufficient to keep the oxide surface clean through energetic ion bombardment. Langmuir probe measurement of the ion current density was used to estimate the bias voltage at the wafer at which this transition took place. For C@sub 4@F@sub 8@, this transition occurs at ~ 60 eV (75 W bias power) in the GEC Cell. At higher bias powers (125 W) where oxide etching is fast (~600 nm/min.), CF@sub 2@ appears to be the key radical for the etch process since ~50 percent (2.7-3.0 mTorr in a 15 mTorr C@sub 4@F@sub 8@ discharge) is consumed. These values were obtained by comparing the CF@sub 2@ concentrations over non-reactive wafer surfaces versus blanket oxide wafer surfaces undergoing etching. CF is shown to display a similar trend, but its concentration is an order of magnitude less than CF@sub 2@, and consequently cannot account on a mass basis for the amount of reactants necessary to balance the amount of etch products. Over a PR surface, neither CF@sub 2@ nor CF concentrations vary as a function of PR etch rate. Consequently, they do not appear to be involved in the PR etch mechanism. However, PR etching is also critically dependent on bias power. PR films etch presumably due to energetic ion bombardment that degrades the PR film, making it liable to attack by fluorine. This project was funded by SEMATECH and NSF

4:20pm **PS1-TuA8 Characterization of Hydrofluorocarbon Reactants for Selective Silicon Nitride Plasma Etch Applications***, **E.A. Hudson**, H. Zhu, D. Pirkle, J. Luque,* Lam Research Corp.*; J.P. Booth,* Ecole Polytechnique, France

Certain dielectric etch applications require the removal of silicon nitride films with high selectivity to silicon dioxide. An important example is found in dual-damascene integration schemes using organic low-k dielectric materials and nitride diffusion barriers. At the completion of the via etch, the nitride at the via bottom must be removed without penetrating the oxide hardmask which protects the top surface of the low-k dielectric film. Nitride-to-oxide etch rate selectivities of >10:1 are desirable. To understand how this selectivity may be achieved, and to compare the effects of different hydrofluorocarbon feed gases, a series of processes have been evaluated using a dual-frequency, capacitively-coupled, dielectric etch system. The feed gases for the processes are Ar and O@sub 2@, combined with a hydrofluorocarbon from the series CH@sub x@F@sub y@, where x ranges from 0 to 4, and y=4-x. Selectivity trends were determined from blanket nitride and oxide etch rates. Trends in the plasma chemistry were characterized using broad-band UV absorption spectroscopy. CF, CF@sub 2@, and CH@sub 3@ densities were measured using absorption bands in the 200-270nm range. This method directly measures absolute densities of ground state radicals in the plasma. Best selectivity results were obtained using CH@sub 3@F, which produced selectivities >20:1 for blanket films and for patterned wafers. The CF@sub 2@ density was found to be relatively high for processes using CHF@sub 3@, and very low for processes using CH@sub 3@F. In contrast, the CF density followed a more linear trend through the hydrofluorocarbon series. Also the production of CH@sub 3@ radical from CH@sub 3@F reactant was much less than from CH@sub 4@ reactant, suggesting that the direct removal of atomic F from CH@sub 3@F is not a favorable dissociation pathway. These results and others are interpreted to understand the mechanism for high nitride-to-oxide selectivity.

4:40pm **PS1-TuA9 Modeling of SiO@sub 2@ Feature Etching in Fluorocarbon Plasmas: The Effect of Gas Phase Composition on Aspect Ratio Dependent Phenomena***, G. Kokkoris, **E. Gogolides,*** National Center for Scientific Research (NCSR) "Demokritos", Greece*; A.G. Boudouvis,* National Technical University of Athens (NTUA), Greece

There are several problems during etching of SiO@sub 2@ features in fluorocarbon plasmas such as Reactive Ion Etching lag (RIE lag), inverse RIE lag,@footnote 1@ and etch stop,@footnote 2@ which have been observed to depend on Aspect Ratio (AR) of the etched feature@footnote 3@ and are included in the general term Aspect Ratio Dependent Etching (ARDE). A goal to achieve in feature etching is Aspect Ratio Independent Etching (ARIE). The context of this work involves modeling of the effect of gas phase composition on AR dependent phenomena during SiO@sub 2@ feature etching in fluorocarbon plasmas. The effort to accomplish this task requires: a) A predictive surface model@footnote 4@ for open area SiO@sub 2@ etching; the surface "coverage", @theta@, is assigned to all species (fluorine atoms, fluorocarbon radicals, and a surface polymer) in the mixed layer created under ion bombardment. The "polymer surface coverage", @theta@@sub P@, could be thought of in a more general sense as a normalized thickness of the polymer overlayer. The model coefficients have been calculated@footnote 4@ by fits to beam experiments' results. b) A model to calculate the local values of neutral and ion fluxes (flux calculator@footnote 5@) inside etched features, which takes into account shadowing of neutral and ion flux and re-emission of neutral flux. Charging effects are not explicitly considered at present. c) A coupling of model (a) with (b) to calculate the local etching rate inside features. The focal point of the coupling is the simultaneous@footnote 5@ calculation of local fluxes and effective sticking coefficients of the neutral species at each elementary surface of the structure being etched. The goal of this work is the prediction of several phenomena (RIE lag, inverse RIE lag, etch stop, and ARIE) and their relation with gas phase composition. A new approach is presented based on maps of two types. The maps of the first type show the effect of gas phase composition on etching yield at the bottom of an etched feature. In the second type of maps the effect of gas phase composition on ARDE and ARIE is illustrated. Gas phase composition is divided into regions characterized by the observation of a specific phenomenon in each region (e.g. RIE lag, inverse RIE lag, ARIE). Furthermore, a preliminary investigation of processes windows satisfying specific demands on ARIE, etching rate magnitude, and etching rate (SiO@sub 2@/Si) selectivity is done. @FootnoteText@ @footnote 1@ M. F. Doemling, N. R. Rueger, and G. S. Oehrlein, Appl. Phys. Lett. 68, 10 (1996). @footnote 2@ O. Joubert, G. S. Oehrlein, and Y. Zhang, J. Vac. Sci. Technol. A 12, 658 (1994). @footnote 3@ R. A. Gottscho, C. W. Jurgensen, and D. J. Vitkavage, J. Vac. Sci. Technol. B 10, 2133 (1992). @footnote 4@ E. Gogolides, P. Vauvert, G. Kokkoris, G. Turban, and A. G. Boudouvis, J. Appl. Phys. 88, 5570 (2000). @footnote 5@ G. Kokkoris, E. Gogolides, A. G. Boudouvis, Etching of SiO@sub 2@ and Si features in fluorocarbon plasmas I: Effect of gas phase composition on aspect ratio dependent phenomena in trenches, submitted for publication to Journal of Applied Physics.

5:00pm **PS1-TuA10 Inductively Coupled Plasma Etching for Arrayed Waveguide Grating Fabrication in Silica on Silicon Technology***, S. Bretoiu, D. Di Mola, E. Fioravanti, **S. Visona***, Agilent Italy

Arrayed Waveguide Gratings (AWGs) in silica on silicon technology were fabricated and tested in our laboratory. The silica optical layers were all deposited in LPCVD furnaces, and waveguide core was etched using a photoresist mask in an inductively coupled plasma source with C@sub 4@F@sub 8@/O@sub 2@/He gas mixture. This article reports the dependence of important process parameters, included aspect ratio dependent etch rate (A.R.D.E.) effect, selectivity and waveguide side wall angle, on RF power, chamber pressure and gas flow rates. In particular the effects of He and O@sub 2@ addition on A.R.D.E. effect and waveguide side wall angle were investigated. Based on these results a reliable and high throughput process was set up to etch silica waveguides suitable for AWG fabrication, with etch rate higher than 300 nm/min, selectivity on photoresist higher than 5:1 and waveguide side wall angle higher than 88.5°. Measurements of first 16 Channel 200 GHz AWGs fabricated with this process are presented and discussed. To conclude preliminary results are reported about etching of high aspect ratio (>3:1) trenches with depths greater than 15 µm, to be used for stress releasing grooves in AWGs.

Plasma Science

Room 104 - Session PS2+TF+SE-TuA

PECVD/IPVD

Moderator: A.B. Bouchoule, University d'Orleans, France

2:00pm **PS2+TF+SE-TuA1 Mechanisms Involved in the PECVD of Thin Films in Low Pressure Organosilicon Plasmas***, **A. Granier**, A. Goullet, K Aumaille, G. Borvon,* Institut des Matériaux Jean Rouxel, France*; C. Vallee,* LEMD, France*; G. Turban,* Institut des Matériaux Jean Rouxel, France **INVITED**

Low pressure organosilicon plasmas are widely used for the deposition of thin organic and inorganic films, used for their dielectric, optical and barrier properties. The organosilicon precursors such as tetraethoxysilane (TEOS), hexamethyldisiloxane (HMDSO) or tetramethylsilane (TMS) are used either pure or mixed with Ar, He, O@sub 2@ or N@sub 2@. The subject of this talk is to present the state of knowledge on the mechanisms involved in the low pressure (1 to 50 mTorr) organosilicon plasmas namely, both homogeneous and heterogeneous reactions. Since the data related to organosilicon reactions are relatively poor, information has to be deduced from experiments. Systematic plasma analyses have been carried out in low pressure RF inductively coupled TEOS and HMDSO based plasma by optical emission spectroscopy, Langmuir probes and mass spectrometry coupled with real time monitoring of the film growth by ellipsometry. It is deduced that electrons are more efficient than O atoms to break HMDSO and TEOS molecules. Organosilicon dissociation rates higher than 90% are easily reached. It is likely that the by-products of the electron impact dissociation are light H and CH@sub 3@ radicals and big fragments directly issued from the organosilicon molecule. On the other hand, in order to get better insight in heterogeneous reactions with O, H atoms, organosilicon film have been exposed to pure Ar, oxygen and hydrogen plasmas. It is demonstrated that oxygen atoms are very efficient to oxidize the organic part of the films, and that a 50 nm thick organosilicon film can be totally transformed into a porous silica film, upon exposition to an oxygen plasma.

2:40pm **PS2+TF+SE-TuA3 Electron Cyclotron Resonance Plasma Enhanced Chemical Vapor Deposition (ECR-PECVD) of ZrO@sub 2@ on Silicon*, B.O. Cho*,** *J. Wang, S.X. Lao, J.P. Chang,* University of California, Los Angeles

ZrO@sub 2@ is one of the most promising high dielectric constant (k) materials to replace SiO@sub 2@ in ultra large scale integration chip fabrication because of its wide band gap and low leakage current level. We developed an ECR-PECVD process to deposit ZrO@sub 2@ with zirconium tetra-tert-butoxide (Zr(OC@sub 4@H@sub 9@)@sub 4@) as an organometallic precursor, Ar as a carrier of the precursor vapor, and O@sub 2@ as an oxidant. Quadrupole mass spectroscopy, optical emission spectroscopy (OES), and Langmuir probe were used to characterize the plasma. The mechanisms of precursor decomposition and oxidation reactions including Zr-ligand bond dissociation and ZrO formation were investigated by analyzing the radical appearance potentials. The decomposition and oxidation reactions in the plasma were mainly controlled by the flow rate ratio of O@sub 2@ to Ar (O@sub 2@/Ar), varying between 0 and 10, and the electron temperature of 2-8 eV with the typical value of 3-4 eV. The OES intensity ratio of C@sub 2@ at 516.52 nm to O at 777.42 nm linearly scaled with the incorporated carbon concentration in the deposited film, which were determined by x-ray photoelectron spectroscopy and secondary ion mass spectroscopy. Since carbon incorporation greatly influenced the electrical performance of the film, low carbon-content, stoichiometric, and amorphous ZrO@sub 2@ was obtained at O@sub 2@/Ar>1 without substrate heating. We also deposited the film at elevated substrate temperatures around 400 °C with the controlled substrate bias to obtain carbon-free amorphous ZrO@sub 2@. The as-deposited ZrO@sub 2@ film between Al electrode and Si in capacitor devices showed good capacitance-voltage and current-voltage characteristics, which yielded k=22 and J=4x10@super -5@A/cm@super 2@ at -1.5 V, respectively. Scanning electron micrograph (SEM) showed that highly conformal film deposition could be achieved over 300 nm diameter cylindrical memory structure with an aspect ratio of 4.

3:00pm **PS2+TF+SE-TuA4 Deposition of a-C:H Films: Plasma Chemistry and Material Properties*, J. Benedikt,*** Eindhoven University of Technology, The Netherlands*; K.G.Y. Letourneur,* Eindhoven University of Technology, The Netherlands, Netherlands*; M. Wisse,* Free University, The Netherlands*; D.C. Schram,* Eindhoven University of Technology, The Netherlands, Netherlands*; M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands

Remote Ar-C@sub 2@H@sub 2@ plasma created by means of a cascaded arc is used for fast rate deposition of hard hydrogenated amorphous carbon films (a-C:H, rate up to 50 nm/s, hardness up to 14 GPa). First the densities of the radicals have been investigated in detail using cavity ring down absorption spectroscopy (CRDS). C@sub 2@, CH, C and H radicals were spectroscopically identified and measured as a function of C@sub 2@H@sub 2@ gas flow admixture. C@sub 2@H radical is still not spectrally resolved but broad band absorption observed around 250, 276 and 431 nm can be ascribed to this radical. The main mechanism of the dissociation of acetylene and other radicals in the plasma is a charge exchange reaction with argon ion and subsequent dissociative recombination of the molecular ion with an electron. Thus the composition of the plasma depends strongly on the amount of argon ions (and electrons) available in comparison with the amount of acetylene molecules injected. A plug-down model of plasma chemistry was made to simulate measured densities and to find creation channels of the different radicals. Second in-situ real time ellipsometry was used during deposition to measure the refractive index and the growth rate of the films. Clear correlation between plasma composition and the properties of the film was observed. Both the refractive index (which is in our case correlated with hardness) and the growth rate increase with increasing acetylene flow. The highest values are reached when the acetylene flow into the chamber is equal or higher than the argon ion flow emanating from the plasma source. In this case the C@sub 2@H radical is dominantly present in the plasma and is the main growth precursor of our films.

3:20pm **PS2+TF+SE-TuA5 Study of SiO@sub x@N@sub y@ Films Deposited by Radio-Frequency Plasma Assisted Electron Cyclotron Resonance*, J.D. Brewer*[1],** University of North Carolina at Chapel Hill*; A. Raveh,* NRCN Division of Chemistry, Israel*; E.A. Irene,* University of North Carolina at Chapel Hill

New techniques for the development of higher dielectric constant materials as a passivation layer of silicon remains a challenge. To this end, a radio-frequency (RF) plasma process, in combination with an electron cyclotron resonance (ECR) plasma, was employed at low pressures (100-1000 mTorr) and low substrate temperatures (100-300°C) to grow silicon oxynitride thin films on p-type Si (100) wafers. N@sub 2@ and O@sub 2@ were used as gas sources to allow separate control of the amount of N and O ions and radicals, thus affording control of film stoichiometry. Films were produced with an ECR power of 300 W and an RF bias range of 0 to -80 V. The ability to tailor film properties such as; composition, interface states, morphology and structure was made possible by varying plasma processing parameters. Spectroscopic ellipsometry, atomic force microscopy, Auger electron spectroscopy, x-ray photoelectron spectroscopy and capacitance-voltage measurements were performed on the silicon oxynitride layers. The nitrogen to oxygen ratio in the silicon oxynitride films was found to depend on competitive processes between N@super +@ and O@super -@ species. Less negative voltages (> -20 V) produced a greater content of oxide due to a larger concentration of O@super -@ ions, while more negative voltages (< -50 V) produced NO and N@super +@ ions and radicals forming a greater content of nitride in the films. In addition, the effects of pressure, flow-rate ratio, time, temperature and ECR power on the fabricated film properties will be presented.

4:20pm **PS2+TF+SE-TuA8 An In Situ Study of the Interactions of Atomic Deuterium with Hydrogenated Amorphous Silicon Thin Films Using Multiple Total Reflection Fourier Transform Infrared Spectroscopy*, S. Agarwal,*** University of California, Santa Barbara*; A. Takano,* Fuji Electric Corporate Research and Development, Ltd., Japan*; M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands*; D. Maroudas, E.S. Aydil,* University of California, Santa Barbara

Atomic hydrogen plays a crucial role in the deposition of amorphous hydrogenated silicon (a-Si:H) from silane containing discharges which are often diluted with hydrogen. However, during the deposition process the role of atomic hydrogen cannot be isolated from the other radicals impinging onto the surface. In order to isolate the effect of H atoms, as deposited a-Si:H films were exposed to a deuterium plasma and subsequent compositional and structural changes in the film were studied using in situ multiple total reflection Fourier transform infrared (MTR-FTIR) spectroscopy. The use of atomic deuterium generated by the plasma allowed us to observe both the abstraction-passivation reaction and the insertion reaction since the stretching modes of SiH@sub x@ (x = 1,2,3) and SiD@sub x@ (x = 1,2,3) appear at different wavenumbers. a-Si:H thin films were deposited in an inductively coupled plasma reactor at 200 °C. The deposited films were exposed to a series of one second deuterium plasma pulses at different substrate temperatures. In situ MTR-FTIR was used to observe the changes in the film after each pulse. Peak assignments were made and the IR data was deconvoluted for both the SiH@sub x@ and SiD@sub x@ part of the spectrum. Removal of surface hydrides is very fast and there is no activation barrier for the abstraction-passivation reaction in agreement with atomistic calculations of this barrier. The modification of the bulk film through abstraction and insertion reactions is limited by diffusion of D. Moreover, we find evidence for the presence of a thin sub-surface region (<30 Å) that has a higher concentration of silicon di- and trihydrides and strained silicon-silicon bonds. Insertion into the Si-SiH@sub2@ bonds in this layer is faster than insertion into Si-SiH.

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[1] **PSTD Coburn-Winters Student Award Finalist**

4:40pm **PS2+TF+SE-TuA9 A New and Fast In-situ Spectroscopic Infrared Absorption Measurement Technique for Submonolayer Detection at High Growth Rate*, M.F.A.M. van Hest*,** *A. Klaver, M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands

Silicon oxide like films are deposited at high rate (up to 200 nm/s) using an expanding thermal plasma (Cascaded arc) in combination with hexamethyldisiloxane (HMDSO) and oxygen as deposition precursors. In general Fourier transform infrared (FTIR) reflection spectroscopy is a useful tool for in situ analysis of the film deposition growth process. However this technique is difficult to apply when the film deposition rate is reaching high values (10 to 100 nm/s). When studying submonolayer growth, the time resolution of a FTIR setup is too long (typical 0.1 - 1 s). So another technique has to be used to improve the time resolution. The heart of the new technique is a grating mounted on a laser scanner, which oscillates at a frequency of up to 300 Hz. Only a small part of the infrared spectrum will reach the detector (MCT). The rotation angle is limited and therefore the spectral bandwidth with respect to a FTIR spectroscope is small (200 cm@super -1@ at 1000 cm@super -1@), but the time resolution improved (1.7 to 10 ms). A cascaded arc is used as a light source, because if its high radiation temperature it produces more infrared light than a glowbar. To make submonolayer absorption detectable, single reflection is not sufficient; therefore attenuated total reflection (ATR) crystals are used as substrates. These crystals make multiple (50) interactions of the infrared beam with the depositing film possible, leading to a higher measured absorption. The set up will be presented in detail as well as the first results of the in situ study of the film growth of silicon oxide like films. Together with the in situ study also a plasma post treatment study has been performed. With this the resistance of the deposited films towards an argon/oxygen plasma has been studied. This study shows that the deposited films contain a significant amount of carbon, which can be removed by post treatment.

5:00pm **PS2+TF+SE-TuA10 Reaction Mechanism of PECVD to Produce Low Dielectric Constant Thin Films*, Y. Shimogaki,*** University of Tokyo, Japan **INVITED**

Ever growing device integration now requires low dielectric constant materials for inter metal dielectrics to improve speed performance of ULSIs. SiO:F (fluorinated silicon oxide) and a-C:F (amorphous fluoro carbon) films produced by PECVD are the major candidates for this purpose. In case of SiO:F film deposition from SiH@sub 4@/N@sub 2@O/CF@sub 4@, we found that fluorine addition to SiO@sub 2@ reduces Si-OH bonds which are the major dielectric component in SiO@sub 2@ films by PECVD. Fluorine addition also reduces growth rate and improved step coverage. We have examined the gas flow rate dependency of the growth rate by keeping the other process parameters constant. The growth rate of SiO:F film increased and the step coverage profile became poor by increasing gas flow rate. We have extracted suitable reaction kinetics to explain these phenomena. The reaction mechanism, which contains two major species in film deposition, obtained from this experimental approach well explained the step coverage behavior. In case of a-C:F film deposition from C@sub 2@F@sub 4@, the film growth rate decreased by increasing the gas flow rate. This is due to the gas phase reactions that produce main film precursors, like as CF@sub 3@@sup +@ ion and CF@sub 2@ radical. We also evaluated the contribution of ionic species and neutral radical species using step coverage into micron scale features. We found that radical species contributes to have uniform step coverage, but most of the film forming species are ionic ones and they contribute to make thermally stable films.

Semiconductors
Room 122 - Session SC+SS-TuA
Semiconductor Nanostructures and Processing

Moderator: D.G. Cahill, University of Illinois, Urbana

2:00pm **SC+SS-TuA1 Nanoparticles for Fabrication of Zero- and One-dimensional Quantum Objects*, L. Samuelson*,** *M. Bjork, K. Deppert, J. Ohlsson, M.H. Magnusson, A. Persson, C. Thelander, R. Wallenberg,* Lund University, Sweden

Quantum dots and quantum wires are of great interest for their possible use in quantum devices, such as single-electron transistors. In many cases these quantum objects are fabricated using different forms of self-organized epitaxial growth. We will report the use of aerosol techniques for fabrication of nanoparticles which are used as building blocks for quantum devices and which also allow us to controllably grow semiconducting, III-V, nanowhiskers. We will first describe our method for controlled fabrication of crystalline nanoparticles of metalli c and semiconducting nanoparticles. Then we will turn to description of the way we grow nanowhiskers or nanoneedles using size-controlled nanoparticles as catalytic seeds which control the dimension and the location of the nanowhiskers. Transmission electron microscope characterization of chemical and structural properties of nanoparticles and nanowhiskers will be presented. Finally we will discuss electrical data from quantum devices obtained via nanomanipulation of nanoparticles and nanowhiskers, a technique that has allowed ohmic electrical contacts as well as tunnel-injecting contacts to be formed to these quantum objects.

2:20pm **SC+SS-TuA2 Growth of Ag Nanowires on Atomically Flat Ag films Formed on GaAs(110) Surfaces*, H.B. Yu*,** *C.-S. Jiang, C.-K. Shih,* University of Texas at Austin

By using the scanning tunneling microscopy, we study the growth and evolution of Ag nanowires on atomically flat Ag films deposited onto GaAs(110) substrates. We show the ability to grow Ag nanowires with a well-defined width and very large aspect ratio (>150:1). For atomically flat Ag-film on GaAs(110), it has been shown that the surface has a quasi-periodic superstructure with long (L) and short (S) wavelength modulations arranged according to the Fibonacci sequence.@footnote 1,2@ We find that for the Ag nanowires grown on such a surface, the width of the nanowires is quantized in units of L (1.7 nm) or S (1.3 nm) segments. Very long (> 1 micron) nanowires of such a well-defined width can be formed on the surface with its ends terminated at the edge of the voids on the Ag film. The formation mechanism and the electronic properties of such nanowires will be discussed. @FootnoteText@@footnote 1@A.R. Smith, K.-J. Chao, Q. Niu, and C.K. Shih, Science 273, 226 (1996). @footnote 2@Ph. Ebert, K.-J. Chao, Q. Niu, and C.K. Shih, Phys. Rev. Lett. 83, 3222 (1999).

2:40pm **SC+SS-TuA3 Ge Nanoclusters Prepared from Solution with Chemically Tailored Surfaces*, B.R. Taylor,*** Lawrence Livermore National Laboratory*; S.M. Kauzlarich,* University of California, Davis*; L.J. Terminello, A.W. van Buuren, C.F.O. Bostedt, T.M. Willey,* Lawrence Livermore National Laboratory

Ge nanoclusters have been prepared by a solution reaction between the Zintl salt Mg@sub 2@Ge and GeCl@sub 4@ in refluxing diglyme@footnote 1@ and triglyme.@footnote 2@ The nanoclusters are produced in a range of sizes from 2 to 10 nm in diameter, and are quantum confined. The particles were characterized by high-resolution transmission electron microscopy and Fourier transform infrared spectroscopy. The shift in band gap of the nano clusters was measured by optical spectroscopy and X-ray photoelectron spectroscopy . @FootnoteText@ @footnote 1@ Taylor, B. R.; Kauzlarich, S. M.; Lee, H. W. H.; Delgado, G. R. Chem. Mater., 1998, v. 10, 22-24. @footnote 2@ Taylor, B. R.; Kauzlarich, S. M.; Lee, H. W. H.; Delgado, G. R. Chem. Mater., 1999, v. 11, 2493-2500.

3:00pm **SC+SS-TuA4 X-Ray Absorption and Emission Studies of Diamond Nanoclusters*, T. van Buuren*,** *J. Plitzko, C.F.O. Bostedt, N. Franco, L.J. Terminello,* Lawrence Livermore National Laboratory

The conduction and valence band structure of bulk diamond and diamond nanoclusters have been measured using x-ray absorption and x-ray emission spectroscopies. The diamond nanoclusters are commercially available products from the Straus chemical corporation and are synthesized in a detonation wave from high explosives. X-ray diffraction and TEM show that the nanodiamond powder is crystalline and approximately 3.5 +/- 1.0 nm in diameter. The nanodiamond K-edge absorption and emission show the same spectral features as bulk diamond with low impurity levels. The C1s core exciton feature clearly observed in the K-edge absorption edge of bulk diamond is not observed in the nanodiamond spectra. A possible explanation for this is a broadening due to a distribution of particle size. The depth of the second gap in the nanodiamond spectra is shallower than that of bulk diamond. This effect has been observed previously and attributed to quantum confinement. We note that no blue shift measured in the position of nanodiamond conduction edge when compared to the bulk diamond contrary to a recent publication that has reported large conduction band shifts in CVD grown diamond nanoclusters.@footnote 1@ Experiments are in progress to measure the nanodiamond conduction band edge from the EELS spectra acquired with a field emission TEM. We compare our conduction band data to the published measurements and comment on the differences. Soft x-ray emission measurements of the valence band structure of the diamond nanocluster will also be presented. The electronic structure of the nanodiamond will be compared to recent results on Si and Ge nanoclusters and the effects of reduced sizes on the electronic structure of group IV semiconductors will be discussed.@footnote 2@ The work is supported by the US-DOE, BES Ma-terial Sciences under contract W-7405-ENG-48, LLNL. @FootnoteText@ @footnote 1@ Y.K. Chang et.al. PRL 82, 5377 (1999). @footnote 2@ van Buuren et.al. PRL 80, 3803 (1998).

3:20pm **SC+SS-TuA5 AFM Tip-mediated Nucleation and Growth of Passivated Au Nanocrystal Islands***, M.D.R. Taylor,* ***P. Moriarty,*** University of Nottingham, UK*; M. Brust,* University of Liverpool, UK

Recent molecular dynamics simulations by Luedtke and Landmann@footnote 1@ have highlighted the rich dynamics associated with diffusion of Au clusters on surfaces. However, although there is a significant amount of work related to the diffusion of clusters formed in gas-aggregation (and related) sources, to date there have been no experimental studies of the dynamic properties of passivated Au nanoparticles@footnote 2@ deposited onto a surface from a colloidal suspension. We report non-contact mode and tapping mode (including phase imaging) atomic force microscopy (AFM) observations of the evolution of close-packed layers of 1.5 nm diameter thiol-passivated Au clusters on SiO2. The morphology of 1.5 nm cluster overlayers differs dramatically to that observed for dodecanethiol passivated clusters of 6 nm diameter.@footnote 3@ Furthermore, during each NC-AFM scan dramatic morphological changes occur - faceted holes develop, islands appear and grow, steps change appearance - which we attribute to strong tip-cluster interactions. Dynamic force-distance spectroscopy curves indicate that instabilities in the feedback loop are responsible for significant mass transport during (nominally) non-contact mode AFM scanning. @FootnoteText@ @footnote 1@ Luedtke WD and Landmann U 1999 Phys. Rev. Lett. 82 3835 @footnote 2@ Brust M, Walker M, Bethell D, Schiffrin DJ and Whyman R 1994 J. Chem. Soc., Chem. Comm. 801 @footnote 3@ Fractal Aggregation of Polydisperse Au Nanoclusters on Silicon, M. D. R. Taylor, P. Moriarty and M. Brust, submitted.

4:00pm **SC+SS-TuA7 Chemically Enhanced Electron Beam Induced Micromachining of SiO@sub 2@***, J.H. Wang, A.R. Guichard, D.P. Griffis,* ***P.E. Russell,*** North Carolina State University

While material removal using chemically enhanced focused ion beam micromachining is well known, utilization of electron beam induced chemistry for material removal is relatively unexploited. If practical techniques can be developed utilizing electron beam induced chemistry for material removal, issues involving the implantation or "staining" by the Ga ion beam generally used for micromachining can be avoided. In this study, the utilization of XeF@sub2@ for electron beam induced selective etching of SiO@sub 2@ is investigated. The influence of electron dose, electron beam energy and XeF@sub2@ pressure is presented. An etch rate of 10nm/sec over a square micron has been achieved at a chamber pressure of 8x10@super -6@ Torr. At low electron beam doses, m aterial is deposited (rather that etched). This deposited material and micromachined features have been characterized by AFM, SEM and EDS. These results clearly demonstrate the ability to micromachine SiO@sub 2@ using XeF@sub2@ enhanced electron beam induced etching.

4:20pm **SC+SS-TuA8 Surface Passivation Effects of Deposited Ge-Nanocrystal Films Probed with Synchrotron Radiation***,* ***C.F.O. Bostedt***[1]*, T. van Buuren,* Lawrence Livermore National Laboratory*; T. Moller,* Hasylab at Desy, Germany*; L.J. Terminello,* Lawrence Livermore National Laboratory

Clusters and nanocrystals represent a new class of materials that exhibit promising novel properties. The production of these nanostructures in the gas phase gives control over not only the size of the nanoparticles, but also over surface passivation â€“ often not possible in other growth modes. The clusters are condensed out of supersaturated Germanium-vapor that is cooled down in a He-atmosphere and are subsequently deposited on a variety of substrates. Their surface is then subsequently passivated with different materials evaporated into the vacuum chamber. This approach allows us to probe in a controlled and dynamic fashion the effect of surface passivation on nanocluster properties. The clusters are spherical in shape and their sizes are determined by atomic force microscopy (AFM) and confirmed by transmission electron microscopy (TEM). X-ray absorption spectroscopy (XAS) was performed on thin films of Germanium (Ge) clusters. We find that the passivating agent strongly alters the electronic structure of the clusters. In general the absorption edge shifts to significantly higher energies compared to cluster films without surface passivation. This can be explained with a stronger confinement effect in the passivated films compared to unpassivated ones due to a reduction of the cluster-cluster interactions. @FootnoteText@ C. Bostedt acknowledges a fellowship from the German Academic Exchange Service DAAD in the HSP-III program, N. Franco from the Spanish Education and Culture Office. The work is supported by the US-DOE, BES Material Sciences under contract W-7405-ENG-48, LLNL.

4:40pm **SC+SS-TuA9 Surface Nanostructuring by Ion Sputtering: The Early Stages***,* ***F. Buatier de Mongeot****, D. De Sanctis, C. Boragno, U. Valbusa,* Universita' di Genova, Italy

Ion sputtering is commonly used in surface science as a standard sample cleaning procedure. Recently, we have demonstrated that prolonged exposure to an ion beam can lead to the formation of regular patterns on surfaces, which have a spatial periodicity in the nanometer range.@footnote 1@ However, it is not trivial to understand how a random process, like the impingement of ions on the surface, can lead to a regular spatial organization.@footnote 2@ In order to investigate this aspect, we studied the early stages of the process by a Variable Temperature Scanning Tunneling Microscope VT-STM. The ion flux was reduced in order to follow the time evolution of the surface self-organization, starting from the single-impact events and until the formation of ripples on an Ag(110) surface occurred. We fixed the ion impact angle to 70 deg from the normal and low substrate temperatures, in order to enhance the erosive contribution.@footnote 1@ Under these experimental conditions, prolonged exposure to the ion beam leads to the formation of a regular ripple pattern parallel to the ion beam direction with a wavelength in the nm range. Surprisingly, in the early stages, after exposing the surface to an ion dose as low as 0.03 ML the surface morphology shows a well defined correlation along the crystallographic directions and only at higher fluences the correlation figure alignes with the ion beam. In this contribution we discuss the relevant parameters of this phenomenon. @FootnoteText@ @footnote 1@ S.Rusponi, G.Costantini, F.Buatier de Mongeot, C.Boragno and U.Valbusa, Appl.Phys.Lett. , 75 (1999) 3318 @footnote 2@ G. Costantini, F. Buatier de Mongeot, C. Boragno and U. Valbusa, Phys. Rev. Lett. 86 (2001) 838.

Semiconductors
Room 124 - Session SC-TuA
Semiconductor Heterojunctions

Moderator: G. McGuire, MCNC

2:00pm **SC-TuA1 Characterization of SiGe/Si Heterostructures with Abrupt Interfaces***,* ***Y. Shiraki,*** The University of Tokyo, Japan **INVITED**

2:40pm **SC-TuA3 Indium Segregation and its Effect on Interfacial Bonding at the GaSb-on-InAs Heterojunction: A Cross-Sectional Scanning Tunneling Microscopy Study@footnote 1@***,* ***J. Steinshnider****, M. Weimer,* Texas A&M University*; E.M. Shaw, Z. Mi, T.C. Hasenberg,* University of Iowa*; R. Kaspi,* Air Force Research Laboratory

We describe how scanning tunneling microscopy (STM) may be used to determine the chemical composition across the nearly-lattice-matched, non-common-atom GaSb-on-InAs heterojunction with atomic-scale precision. An ideal, compositionally-abrupt GaSb-on-InAs interface is composed of either InSb-like or GaAs-like bonds whose character is easily distinguished with STM.@footnote 2@ Indium segregation, on the other hand, leads to compositional grading within the subsequent GaSb layers that compromises interfacial abruptness. We have quantified the indium fraction in successive gallium planes and find this compositional grading is described by the same microscopic model previously applied to antimony segregation at the InAs-on-GaSb interface.@footnote 3@ We discuss how indium segregation at the GaSb-on-InAs heterojunction is linked with the surface reconstruction of the underlying InAs template and consider the effect of this segregation on the interfacial bonding. @FootnoteText@ @footnote 1@Work supported by the National Science Foundation (Division of Materials Research) and Air Force Research Laboratory @footnote 2@J. Steinshnider, M. Weimer, R. Kaspi, and G.W. Turner, Phys. Rev. Lett., 85, 2953 (2000). @footnote 3@J. Steinshnider, J. Harper, M. Weimer, C.-H. Lin, S.S. Pei, and D.H. Chow, Phys. Rev. Lett., 85, 4562 (2000).

3:00pm **SC-TuA4 Dislocations and Microstructure Evolution in Semiconductor Thin Films***,* ***A. Sakai,*** Nagoya University, Japan **INVITED**

The utilization of high-quality heteroepitaxial films is the key to realizing high performance optoelectronic and electronic semiconductor devices. In general, a lattice mismatch between a heteroepitaxial film and a substrate induces strain into the film and the strain relaxation is achieved by the

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[1] **Morton S. Traum Award Finalist**

introduction of misfit dislocations. This, in most cases, results in threading dislocations in the film, which severely degrade the properties required for the device operation. In order to reduce the threading dislocation density, we have performed novel heteroepitaxy which is based on the idea that misfit dislocations are confined at the hetero interface regions without leaving their threading arms in the film. Two successful demonstrations for GaN and SiGe thin films are presented. 1) Facet-initiated epitaxial lateral overgrowth (FIELO) allows us to obtain GaN films on sapphire substrates with threading dislocation densities on the order of 10@super 7@ cm@super -2@ which is two orders of magnitude smaller than that of the conventional epitaxy. Transmission electron microscopy analyses revealed that the reduction of the threading dislocation density was mainly due to dislocation bending in the FIELO GaN layer. Mechanisms of dislocation propagation which is closely related to the appearance of the facets early in ELO are discussed. 2) Strain-relaxed SiGe buffer layers on Si(001) substrates with low threading dislocation densities have been grown. The process consists of annealing of the first low-temperature-grown SiGe layer and growth of the second SiGe layer on the first layer. A thin capping Si layer formed before the annealing effectively suppressed surface roughening during the annealing. Periodic undulation was formed on the second layer surface, conformably to the alignment of interface misfit dislocations. This undulation plays an important role in introducing the dislocations uniformly and in suppressing the entanglement of threading arms of the dislocations.

3:40pm **SC-TuA6 The Strain Relaxation Mechanism of SiGe Growth with a Low Temperature Si Buffer Layer by Molecular-beam Epitaxy***, **S.W. Lee,*** National Tsing Hua University, Taiwan, R.O.C.*; Y.H. Peng,* National Taiwan University, Taiwan, R.O.C.*; H.C. Chen,* National Tsing Hua University, Taiwan, R.O.C.*; H.H. Cheng, C.H. Kuan,* National Taiwan University, Taiwan, R.O.C.*; L.J. Chen,* National Tsing Hua University, Taiwan, R.O.C.

Recently, the use of the low temperature Si (LT-Si) buffer layer to achieve dislocation-free SiGe films was found to be effective to share the mismatch strain in epilayers. However, the mechanism of strain relaxation in a LT-Si buffer layer has not been well understood. In the present work, the growth of 300-nm-thick Si@sub0.7@Ge@sub0.3@ films with a LT-Si buffer layer grown at 550°C~350°C and with thickness of 50nm~250nm have been carried out by molecular-beam epitaxy. The SiGe films were characterized by transmission electron microscopy (TEM), double-axis x-ray diffraction (DAXRD), atomic force microscopy (AFM) and photoluminescence (PL). From DAXRD measurement, Si@sub0.7@Ge@sub0.3@ films with a 100-nm-thick LT-Si buffer layer grown at different temperatures were found to be fully relaxed (100%). However, Si@sub0.7@Ge@sub0.3@ films became partially relaxed with increased thickness of LT-Si buffer layers. From cross-section TEM (XTEM) observation, the microstructures of LT-Si buffer layers change with deposition temperature and thickness of LT-Si layers. XTEM images showed that the distribution of dislocations formed in the LT-Si buffer layer is correlated with the degree of relaxation. The strain relaxation mechanism is explained in terms of the compliant effect of LT-Si buffer. A novel method based on this mechanism using a thin Ge layer interposed below the LT-Si buffer layer for Si@sub0.7@Ge@sub0.3@ growth is demonstrated. The interposed Ge layer plays a critical role in leading the misfit dislocations to transverse along the LT-Si/Si interface. Controlling misfit dislocations in LT-Si buffers was achieved. The interposed Ge layer was expected to promote the relaxation of the top SiGe films.

4:00pm **SC-TuA7 Heteroepitaxy of Highly Mismatched Systems and the Role of Coincidence Lattice***, **K.H. Ploog,*** Paul Drude Institute for Solid State Electronics, Germany **INVITED**

While till mid 1980 a good lattice match of substrate and constituent layers in most semiconductor heterostructures was considered to be mandatory for successful device operation, this constraint has since become more relaxed. Today not only semiconductor materials with considerable lattice mismatch are explored in devices, but also heterostructures combining materials very dissimilar in structure, bonding, and chemical properties play an ever increasing role in the development of novel device concepts. In the heteroepitaxy of such highly mismatched systems, the existence of a "coincidence" lattice at the interface often leads to a unique epitaxial alignment and misfit accommodation in the early stages of epitaxy. This structural coincidence between the adjacent lattices helps to generate a low-energy interface. Using functional selforganized molecular beam epitaxy (MBE), even the epitaxy of metastable phases (like cubic GaN-on-GaAs), of M-plane oriented GaN[GaN(1-100) on g-LiAlO2(100)], and of layers with a symmetry different from the substrate (like hexagonal MnAs on cubic GaAs) can be obtained and the resulting nanostructures at the respective interface can be controlled in a reproducible manner. The M-plane group-III nitride heterostructures are of great importance for highly efficient blue/UV light emitters, and ferromagnetic MnAs on GaAs heterostructures are paving the way to spin-electronics operating at room temperature.

4:40pm **SC-TuA9 Nanoscale Dislocation Patterning in PbTe/PbSe (001) Lattice-mismatched Heteroepitaxy***, G. Springholz, **K. Wiesauer,*** University of Linz, Austria

Molecular beam epitaxy of PbTe on 5.2% lattice-mismatched PbSe (100) is studied using scanning tunneling microscopy. It is found that at a critical thickness of 0.8 monolayers, pure edge type misfit dislocations are formed at the layer/substrate interface. In the STM images these misfit dislocations appear as dark lines that run over the epitaxial surface along the four-fold directions. From atomically resolved lattice images, the dislocation Burgers vector is found to be ½ parallel to the interface. This unusual misfit dislocation configuration is explained by the fact that the dislocation are formed by climb rather than glide processes. From detailed investigations of the early relaxation stages, we find that all misfit dislocations are all injected from monolayer step edges on the surface, which greatly reduces the nucleation barrier of dislocation half loops. As the layer thickness increases, the dislocation density drastically increases and a nearly perfect quadratic grid of dislocations with an average spacing of 10 nm is formed, indicating that at 10 ML more than 90% of the misfit strain is relaxed. In addition, the course of strain relaxation is found to be in well agreement with the Frank-van-der-Merwe model. This surprising result is explained by the reduction of the dislocation nucleation barrier by the edge injection mechanism. The remarkable uniformity of the dislocation array is evidenced by the appearance of satellite peaks in the FFT power spectra of the STM images due to the dislocation superstructure. From a statistical analysis we find a variation of the lateral dislocation spacing of only 12%, which is better than the typical size uniformity of self-assembled quantum dots. Thus, these structures could serve as templates for the deposition of self-organized ordered nanostructures.

5:00pm **SC-TuA10 STM-Controlled Epitaxy of Cobalt-Semiconductor Compounds***, **I. Goldfarb,*** Tel Aviv University, Israel*; G.A.D. Briggs,* Oxford University, UK

Metal-semiconductor compounds play a key role in micro- and optoelectronic devices, mostly as contacts and interconnects. At present, the most popular are the silicides of Ti, and even more so of Co (due to its suitability for self aligned process). However both CoSi@sub 2@ and TiSi@sub 2@ are usually used in a form of polycrystalline thin films. While monocrystalline epitaxial growth of TiSi@sub 2@ on silicon is impeded by its large lattice mismatch between them, it could have been expected for the CoSi@sub 2@ in view of the latter's low mismatch with silicon. Obviously, monocrystalline contacts with improved electrical characteristics are highly desirable. Yet, CoSi@sub 2@ does not grow on silicon as a moncrystalline two-dimensional layer, at least not on the Si(001) surface, where CoSi@sub 2@ forms misoriented three-dimensional islands. CoGe@sub 2@ is another interesting metal-semiconductor compound that can be used, for example, as contacts to SiGe alloys and GaAs. CoGe@sub 2@ forms three-dimensional islands on Ge/Si(001), which are very similar to the CoSi@sub 2@ ones on Si(001). In this work we investigate the mechanisms of CoSi@sub 2@ and CoGe@sub 2@ growth by carefully-controlled e-beam evaporation of Co onto Si(001) substrates, as monitored in situ, from the very initial submonolayer stages, by scanning tunneling microscopy (STM) and reflection high-energy electron diffraction (RHEED). In order to affect the resultant epilayer morphologies, we use flat and vicinal surfaces, and two different ways of synthesis: reactive deposition (where Co is deposited onto hot substrate), and solid-phase reaction (where Co is deposited at lower, or room temperature). We attempt to account for the observed morphological differences of the epilayers by correlating them with the above-mentioned parametric differences.

5:20pm **SC-TuA11 Electron-beam Patterning of Cobalt Fluoride on 10-nm Length Scale***, **M. Malac**, Y. Zhu, M. Schofield,* Brookhaven National Laboratory

Electron-beam modification of a precursor material can be utilized to fabricate metallic structures on single-digit nanometer dimensions. Whereas, reliable fabrication of magnetic nanostructures is essential for study of fundamental processes in magnetism, cobalt fluoride (CoF2) precursor is a candidate for such fabrication of magnetic (cobalt) nanostructures. We have studied in situ electron beam patterning of CoF2 using a JEOL 3000F transmission electron microscope. The microscope is equipped with a Gatan Image Filter allowing for electron-energy-loss chemical analysis, and equipped for electron holography for mapping of magnetic fields. Our results on electron beam (<10 nm probe) modification of cobalt fluoride show that electron dose typically of 900 C/cm2 is needed for complete removal of fluorine at temperature 570 K. However, cobalt particles about 3 nm in diameter start to form at electron doses on the order of 200 C/cm2. Nucleation of cobalt particles initiates at the grain boundaries of the CoF2 precursor. The Co particles grow during exposure resulting, after complete exposure, in structures composed of separated, faceted cobalt particles typically 5 - 15 nm in size. The cobalt particles are either c-axis parallel or perpendicular to the substrate plane. Elevated sample temperature during exposure was necessary to eliminate buildup of microscope-related contamination. Cooling the sample to liquid nitrogen temperature during exposure also resulted in elimination of microscope contamination, but the resulting cobalt structures were composed of individual, separated particles. We believe that the non-continuous nature of the final cobalt structures stems from the surface energetics of high surface energy metal (cobalt) on low surface energy substrate (amorphous carbon). A real-time high-resolution TEM movie of the exposure process will be presented to provide insight to the exposure process.

Surface Engineering
Room 132 - Session SE-TuA
Hard and Superhard Coatings

Moderator: I. Petrov, University of Illinois, Urbana

2:00pm **SE-TuA1 Microstructure and Mechanical Properties of Zr-Si-N Films Prepared by r.f.- Reactive Sputtering***, **M. Nose,*** Northwestern University, Japan*; W.A. Chiou,* University of California at Irvine*; M. Zhou,* Osaka University, Japan*; T. Mae,* Toyama National College of Technology, Japan*; M. Meshii,* Northwestern University

ZrN and ZrSiN films were prepared in an r.f. sputtering apparatus which has a pair of targets facing each other (referred to as the Facing Target -type r.f. Sputtering). Films were deposited on silicon wafer without bias application nor substrate heating in order to examine only the effect of silicon addition to transition metal nitride films. The transmission electron microscopy studies were carried out in addition to XRD. For the high resolution TEM observation, the field emission type transmission electron microscope (FE-TEM) was used, which provides a point-to-point resolution of 0.1nm. The samples were observed both parallel and perpendicular to the film surface, which were in-plane and cross-sectional view, respectively. In order to investigate the relationship between mechanical properties and microstructure of films, the hardness was measured by a nano-indentation system at room temperature. The load was selected to produce an impression depth below 60nm (not more than 5% of film thickness) so that the influence from the substrate can be neglected. The contents of zirconium, nitrogen and silicon of the films were determined by ZAF method with EPMA. A study of their microstructure and mechanical properties has provided as follows: (1) The hardness and Young's modulus increase with small Si additions reaching maximum values of 35GPa (at 3%Si) and 370GPa (at 5% Si), respectively; (2) The hardest films containing 3%Si did not consist of nano-crystals but clear columnar crystals in the range of 10 to 25nm; (3) The increment of hardness with small amount of Si atoms can be attributed to the solution hardening by Si to ZrN lattice; (4) In the case of ZrSiN films deposited by r.f. sputtering without bias application nor substrate heating, the available result did not ensure the presence of ZrN nano-crystals embedded in Si@sub 3@N@sub 4@ matrix.

2:20pm **SE-TuA2 Characterization of CrBN Films Deposited by Ion Beam Assisted Deposition***, S.L. Rohde,* ***S.M. Aouadi****, D.M. Shultze, T.Z. Gorishnyy,* University of Nebraska - Lincoln*; N. Finnegan,* University of Illinois at Urbana-Champaign

This paper reports on the first attempt to grow and analyze CrBN nanocrystalline materials using physical vapor deposition processes. Coatings were deposited at low temperatures (<200 Â°C) on silicon substrates using ion beam assisted deposition (IBAD). These coatings were characterized post-deposition using X-ray diffraction (XRD), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), infrared spectroscopic ellipsometry (IR-SE), and visible-light spectroscopic ellipsometry (VIS-SE). The primary phases in the films were identified using XRD. The surface morphology and nanocrystalline nature of the coatings (grain size of 5 - 7 nm) were deduced using AFM. The mechanical properties (wear rate, hardness, elastic modulii) of the coatings were evaluated using a nanohardness test. The chemical composition and phase composition of the samples were determined from XPS and AES measurements and were subsequently deduced from the analysis of the VIS-SE data. The film compositions deduced from both techniques correlated well. Additionally, XPS, AES, and IR-SE were used to reveal the crystal structure of the BN phase in these ternary compounds.

3:00pm **SE-TuA4 Thin Film Growth by Physical Vapor Deposition in the Presence of Residual Gas***, **J.M. Schneider,*** Linkoping University, Sweden **INVITED**

Vacuum based techniques are characterized by the presence of residual gas. Depending on the affinity of the residual gas to the growing film material, chemical reactions may be possible. Residual gas based impurity incorporation during thin film growth has been reported previously.@footnote 1,@@footnote 2@ Here, the state of the art in residual gas - growing film interactions is reviewed. Sources for residual gas incorporation as well as incorporation mechanisms are described. Furthermore the effect of impurity incorporation on the film structure and film properties are discussed. @FootnoteText@ @footnote 1@ J.M.Schneider et al, Appl.Phys.Lett. 74, 200 (1999). @footnote 2@ J.M.Schneider et al, Appl.Phys.Lett. 75, 3476 (1999).

3:40pm **SE-TuA6 Boron and Boron-Based Coatings as Produced by Vacuum Arc Technology***, **C.C. Klepper,*** HY-Tech Research Corporation*; J.M. Williams,* Oak Ridge National Laboratory*; R.C. Hazelton, E.J. Yadlowsky, E.P. Carlson, M.D. Keitz,* HY-Tech Research Corporation

In principle, boron as a material has many excellent surface properties, including corrosion resistance, very high hardness, refractory properties, and a strong tendency to bond with most substrates. However, the potential technological benefits of the material have not been realizable because of difficulty in synthesis of coatings. Boron is difficult to evaporate, does not sputter well and cannot be thermally sprayed. In the present program, a robust system, based on the vacuum (cathodic) arc technology, for generation and delivery of boron plasmas to substrates has been developed. The system produces a fully-ionized boron plasma, which allows use of substrate bias to control the energetics of deposition. Films and coatings have been produced on 1100 Al, CP-Ti, Ti-6Al-4V, 316 SS, hard chrome plate, 52100 steel and other materials. Analyses have been performed by Rutherford backscattering spectrometry. Properties are being evaluated by nanoindentation hardness and other techniques. First results are that the coatings are smooth, highly adherent, and pore free. A number of applications are contemplated. @FootnoteText@ @footnote 1@ Research sponsored in part by the National Science Foundation under contract # DMI-0078385 with HY-Tech Research Corporation. Research at Oak Ridge National Laboratory is sponsored by the U. S. Department of Energy under contract # DE-AC05-00OR22725 with UT-Battelle, LLC.

4:00pm **SE-TuA7 Ion-bombardment Induced Phase Transformation of Cubic Boron Nitride Studied by Reflection Electron Energy Loss Spectroscopy***, **Y.Y. Hui**, K.W. Wong,* Chinese University of Hong Kong, P.R. China*; W.M. Lau,* Chinese University of Hong Kong, P.R. China, People's Republic of China

The phase transformation of cubic boron nitride (c-BN) in the near surface region of a c-BN (111) facet induced by low energy argon ion bombardment has been investigated by reflection electron energy loss spectroscopy (REELS), with the objective of tracking possible growth mechanisms of c-BN in ion assisted vapor deposition. By removing Tougaard background of the REELS spectra, we can quantitatively measure the percentage of different BN phases on c-BN surface after ion bombardment. In addition, varying the energy of the incident electron beam from 250 eV to 650 eV allowed the adjustment of sampling depth of a c-BN surface from 14 Å to 27 Å. It was found that with an ion energy of 500 eV at a fluence of 5 x 10@super 16@ ions/cm@super 2@, 76 % of c-BN was found transformed to h-BN and a-BN in a top surface layer of 8 Å. Lowering down the argon bombardment energy to 200 eV reduced the defective layer thickness to 5 Å. A damage saturation was observed at a fluence of 6 x 10@super 16@ ions/cm@super 2@, at which about 10% of c-BN was transformed into non-cubic phases. Through further investigations on the damage saturation at other ion energies, the effects of ion beam bombardment on a c-BN surface was comprehensively studied. The present work gives, for the first time, a quantitative explanation of the difficulty in growing pure c-BN films with ion assisted deposition and the presence of an upper-bound in ion energy above which h-BN and a-BN are generated.

4:20pm **SE-TuA8 Cubic Boron Nitride Thin Films Deposited on Steel Substrates With Different Interlayers**, *M. Ye, **M.P. Delplancke-Ogletree**,* Universite Libre de Bruxelles, Belgium

Cubic boron nitride thin films were deposited on steel substrates using electron cyclotron resonance plasma enhanced chemical vapor deposition. Different interlayers, such as BCN, TiBN, Ti, TiN, and hexagonal boron nitride, were investigated regarding to the promotion of cubic boron nitride growth and the improvement of the film mechanical properties. A systematic optimization procedure for the cubic boron nitride formation was carried out regarding the deposition conditions, including the gas composition, substrate temperature, bias voltage. The films were characterized using Fourier transform infrared spectroscopy, transmission electron microscopy, x-ray photoelectron spectroscopy, and atomic force microscopy. It was found that among the different interlayers, hexagonal boron nitride gives the best results.

4:40pm **SE-TuA9 Industrial Laser-Arc Coater for the Deposition of Superhard Amorphous Carbon Films (Diamor)**, ***T. Schuelke**, H.J. Scheibe, P. Siemroth, B. Schultrich,* Fraunhofer Institute for Materials and Beam Technology

Thin amorphous carbon films (Diamor), deposited through laser-assisted cathodic arc evaporation (LaserArco process), have shown unique properties of great relevance to engineered surfaces for wear and corrosion protection. The high-modulus (> 600 GPa) coatings are superhard (80GPa) with a low coefficient of friction (0.1 dry against steel). The vast variety of potential applications includes cutting and forming tools as well as components in rolling or sliding contact situations. The LaserArco plasma source and the Diamor deposition process have proven to be consistently reliable on the laboratory scale. Extended application development yielded to an increasing demand for the Diamor coating. Subsequently, the further development aimed at scaling up the technology to industrial dimensions. This development included the design of a flexible and compact plasma source module, which was then integrated into a high volume production coater. The paper discusses the equipment design and capabilities, integration and process transfer issues, and first deposition results obtained in an industrial environment.

5:00pm **SE-TuA10 Deposition of Diamondlike Carbon by Magnetic Pole Enhanced Inductively Coupled Plasma**, *T. Meziani, P. Colpo, G. Ceccone, P. Leray, P.N. Gibson, D. Summa, **F. Rossi**,* Joint Research Center, Italy*; P. Ranson,* GREMI, CNRS-Universite d'Orleans, France

The ICP sources are particularly interesting for the deposition of amorphous carbon since they offer the possibility to control independently the ion energy from the ion flux bombarding the substrate, in contrast to capacitively coupled discharge. Diamondlike carbon coatings (a-C:H) were deposited with a novel inductively coupled plasma source (the Magnetic Pole Enhanced ICP or MaPE-ICP) designed and characterized in our laboratory. The MaPE-ICP uses a magnetic pole to concentrate the magnetic flux on the load (i.e. plasma) and shows very interesting features like high plasma density, good plasma uniformity and wide pressure range. Diamondlike carbon coatings were deposited with this source from CH4 and C2H2 precursors. The plasma was studied by Langmuir probe measurements, optical emission spectroscopy and microwave interferometry. Mass spectrometry including ion detection and ion energy distribution measurements have been carried out at the substrate holder surface in order to investigate directly the impinging species on the growing film. The plasma diagnostics and films characterization including FTIR spectroscopy, Raman spectroscopy, and X-ray reflectivity (XRR) were undertaken for various processing parameters. The results were related to the coating properties like hardness and intrinsic stress.

Surface Science
Room 120 - Session SS+BI-TuA
Poirier Memorial Session: Self-Assembled Monolayers II

Moderator: M.J. Tarlov, NIST

2:00pm **SS+BI-TuA1 Self-Assembling Monolayers and Thin-Film Templates - Driven Assembly of Functional Organic Structures**, ***R.G. Nuzzo**,* University of Illinois at Urbana-Champaign **INVITED**

The properties of complex matter and assemblies follow from structural elements embedded at a variety of length scales. These influences begin at the most microscopic level--that is at sizes associated with the atomic or molecular constituents--and extend upwards through increasingly more complex hierarchies of organization. While it is common in research to focus on organizations that arise via a thermodynamically directed assembly, it is now possible to design and study assemblies that form solely as a result of the temporal evolution of the underlying dynamics of the system. In this talk I will explore these ideas, focusing on the important role played by dynamics in prototypical complex organic thin-film assembly systems. Specific attention will be given to thin film systems that develop interesting mesoscopic organizations as a result of driven processes occurring at a substrate surface.

2:40pm **SS+BI-TuA3 Adsorption and Photoinitiated Chemistry on Organic-functionalized Semiconductor Surfaces**, ***N. Camillone III**, K. Adib, R.M. Osgood, Jr.,* Columbia University

Greg Poirier's pioneering imaging work had a specific and important role in the scientific and intellectual development of one of the authors (N.C.), and played an instrumental part in the growth of our understanding of the structure and dynamics of self-assembled monolayers. Many experiments have been conceived based upon this understanding. We report results of one such experiment, which characterizes the growth and photoinitiated chemistry of methyl bromide monolayers adsorbed at the surface of short-chain thiolate monolayers on GaAs(110) surfaces. The thiolate monolayers are grown in UHV by exposure of the GaAs to alkyl disulfides. Temperature programmed desorption reveals that the CH@sub 3@Br-surface interactions are strongly modified by the presence of the thiolate spacer layer. With increasing chain length, the CH@sub 3@Br becomes progressively less tightly-bound. The simple layer-by-layer growth behavior observed on bare GaAs(110) is lost, and CH@sub 3@Br appears to form clusters at critical coverages. Exposure to 248 nm light results in the dissociation of the CH@sub 3@Br, most likely due to the dissociative attachment of excited substrate electrons. The cross section for the reaction is strongly enhanced in the case of the ethyl disulfide spacer layer. The implications of the results will be discussed within the context of electron transport through molecular spacers, adsorbate affinity level shifts, and deexcitation mechanisms.

3:00pm **SS+BI-TuA4 Photoinduced Processes in Self-Assembled Monolayers on Semiconductor Surfaces**, ***T. Ye**, E. McArthur, E. Borguet,* University of Pittsburgh

The photoreactivity of ODS(Octadecylsiloxane) SAMs on semiconductor surfaces under UV illumination in air, has been investigated by a combination of contact angle, FTIR and AFM. This work provides strong evidence that SAM degradation does not result from ozone alone. A combination of UV and oxygen is necessary for monolayer degradation to proceed. AFM measurements on submonolayer coverage SAMs provide direct evidence of the degradation of ODS SAMs and reveal the role of defects in the degradation process. FT-IR and AFM results suggest that the hydrocarbon chain is the reactive site of the monolayers. A microscopic mechanism of the degradation involving hydrogen abstraction is suggested based on the mechanism of gas-phase oxidation of alkanes. These results have implications for photoresist micropatterning and nanotechnology applications that require high spatial resolution.

3:20pm **SS+BI-TuA5 Organic Monolayers on Silicon and Silica Surfaces Via Covalent Linkages**, ***X.-Y. Zhu**,* University of Minnesota **INVITED**

Monolayer assemblies on silicon and silica surfaces are of interest for a number of technological reasons, such as substrates in micro-arrays, surface passivation in MEMS, and monolayer mask in soft-lithography. I present novel approaches for the formation of molecular monolayers on silicon and silica surfaces. These approaches rely on a two-step strategy: in the first step, a silicon or silica surface is activated to give reactive functional groups; in the second step, the activated surface reacts with simple organic molecules for monolayer assembly. Examples of alkyl, aromatic, and PEG monolayer assemblies will be presented and their applications in MEMS and micro-arrays will be demonstrated.

4:00pm **SS+BI-TuA7 Study of Alkylsilane Monolayers Islands on Mica in the Presence of Water**, ***M. Luna**,* Lawrence Berkeley National Laboratory*; I. Diez, F. Teran, F. Sanz,* Universitat de Barcelona, Spain*; D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory

The increasing interest in the study of self-assembled monolayers for the last two decades is related to their potential in different fields of science and technology such as biological sensors, @footnote 1@ optoelectronics,@footnote 2@ tribology@footnote 3@ and corrosion inhibition. @footnote 4@ The knowledge of the stability of the packing, the electrostatic and dielectric properties, and the understanding of the formation process of SAMs constitute crucial phenomena to be investigated in the presence of a changing relative humidity atmosphere.

Thus we have performed several series of experiments on alkylsilane monolayer islands vs. relative humidity by means of Polarization Force Microscopy and Dynamic Force Microscopy. The results show that the autoorganizacion is achieved starting from a layer where the molecules are lying down. Also, due to the hydrophilic properties of the alkylsilane monolayer islands, water adsorbs only on mica. This produces an important increase of the dielectric constant on the mica which, in polarization force microscopy, reverses the topographic contrast at around 30% and reaches a maximum at 80%. In addition, by measuring the relative topographic distance between the mica and the islands we are able to quantify the amount of water adsorbed on mica at high relative humidity. . @FootnoteText@ @footnote 1@ K. Shierbaum, T. Weiss, E. T. van Velzen, J. Engbersen, D. Reinhoudt and W. Göpel, Science 265, 1413 (1994). @footnote 2@ A. Ulman, Thin Films: Self-Assembled Monolayers of Thiols, Academic Press, New York, 1998. @footnote 3@ J. I. Siepmann and I. R. McDonald, Phys. Rev. Lett. 70, 453 (1993). @foornote 4@ F. Zamborini and R. Crooks, Langmuir 14, 3279 (1998).

4:20pm **SS+BI-TuA8 "Interphase" Liquid Structure and Interfacial Forces*, H.I. Kim*, *J.E. Houston,* Sandia National Laboratories

There is growing evidence that liquids behave differently within nanometer-proximity to surfaces due to the formation of quasi-ordered "interphase." Understanding the correlation between the surface chemistry, the interphase structure and the resulting in terfacial forces between neighboring surfaces is of fundamental importance to various aspects of nano-scale materials research, including biomaterials, nanotribology and microelectromechanical (MEMs) devices. We use interfacial force microscopy (IFM) to q uantitatively measure interfacial bonding and frictional forces in order to identify the correlation between surface chemistry and interphase sturcture. We outline the results from two systems. In the first, we measure forces between a gold tip and sample, both coated with oligo(ethylene glycol)-terminated SAMs, in water. We observe anomalous interfacial forces due to the interphase water layer, which dominates the interfacial properties. It has been suggested that the interphase water is responsible for the protein-resistant nature of this SAM surface. In the second, we use a long-chain hydrocarbon liquid, hexadecane, which is known to form an ordered layer on a flat metal surface (e.g., gold). We find that this ordered layer passivates the interfacial i nteraction of a tungsten tip with a gold surface even under high stresses. The structure of this layer can be perturbed by applying an electric field and results in extended frictional forces without significant changes in the behavior of the normal-force. These results will be discussed in terms of the interfacial chemistry and the structure of the interphase liquid. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under a Contract DE-AC04-94AL85000.H. H.

4:40pm **SS+BI-TuA9 Alkanethiols on Copper Single Crystal Surfaces*, S. Vollmer*, *G. Witte, C. Wöll,* Ruhr-Universität Bochum, Germany

Ultrathin organic films of self-assembled molecules (SAMs) have attracted considerable interest because of their promising technical applications. Whereas the vast majority of related studies have been focused on alkanethiolate (C@sub n@) films on gold surfaces, which are considered as prototype systems, the structure and properties of SAMs on transition metal surfaces are by far less intense studied. Here we present the results of a comprehensive study of the formation and structure of alkanethiol monolayers of various chain length (n @<=@ 12) on the low indexed copper surfaces [i.e. (111), (100) and (110)]. The films which have been prepared by gas phase adsorption under UHV conditions were characterized by means of XPS, TDS, LEED and HAS. At low temperatures alkanethiol molecules are physisorbed with their molecular axis parallel to the surface without any long range ordering. With increasing temperature (110-250K) a conversion into a copper thiolate species takes place depending on the alkyl chain length which is accompanied by an upright tilting of the molecules. Upon adsorption at room temperature highly ordered thiolate monolayers are observed of which structures depend only on the substrate orientation but not on the chain length. Heating the films above 380K causes a S-C bond cleaving and desorption of the entire alkyl chains leaving the S-atoms on the surface. Surprisingly, the saturation structures are metastable and decompose already at about 250K upon partial desorption of the alkyl chains into a thermodynamically stable mixture of thiolate and sulfide species. The presently observed differences to the case of SAMs on gold surfaces are attributed to the much stronger S-Cu interaction.

5:00pm **SS+BI-TuA10 Electro-Rheology of Liquid Hexadecane Near a Au Surface*, J.E. Houston*, *H.I. Kim,* Sandia National Laboratories

In an earlier study we showed that C10 and C12 alkanethiol self-assembled monolayers on Au surfaces conduct only with significant applied stress and that the friction increases along with the increasing current, indicating significant changes in both structural and electronic properties of the film. In this presentation we outline results from a similar interfacial force microscope (IFM) study of hexadecane films near a Au(111) surface immersed in liquid. At room temperature, hexadecane forms mechanically stable surface multi-layers, which also inhibit conduction. However, under an applied electric field, the film structure is perturbed causing friction forces at extended separations but with no significant repulsion. We discuss these findings in terms of both the molecular and dielectric properties of the films as well as the effect of liquid temperature. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin company, for the DOE under Contract DE-AC04-94AL85000.

Surface Science
Room 121 - Session SS-TuA
Metal Oxides: Structure and Photocatalysis

Moderator: C. Noguera, Universite Paris Sud

2:00pm **SS-TuA1 Scanning Tunneling Microscopy Study of the Reduced Fe@sub 3@O@sub 4@(111) Terminated Selvedge on a Natural Single Crystal @alpha@-Fe@sub 2@O@sub 3@(0001) Surface: Termination and Surface Reaction with Carbon Tetrachloride*, K.T. Rim*, *J.P. Fitts, T. Muller, K. Adib, N. Camillone, R.M. Osgood,* Columbia University*; S.A. Joyce,* Pacific Northwest National Laboratory*; G.W. Flynn,* Columbia University

Scanning Tunneling Microscopy(STM) and Low Energy Electron Diffraction(LEED) have been used to study the degradation of CCl@sub 4@ on the reduced surface of a natural @alpha@-Fe@sub 2@O@sub 3@(0001) surface. STM and LEED results indicate that repeated cycles of Ar@super +@ sputtering at 2kV and annealing in vacuum and in 10@super -6@Torr of O@sub 2@ partial pressure at 850K reduces the @alpha@-Fe@sub 2@O@sub 3@(0001) surface. Based on STM images approximately 90 % of the reduced surface is terminated by Fe@sub 3@O@sub 4@(111), while the remaining 10 % is terminated by FeO(111) and an unidentified phase. CCl@sub 4@ vapor was dosed on the reduced surface at room temperature. STM images were obtained at room temperature before and after the surface was exposed to CCl@sub 4@. STM images before dosing CCl@sub 4@ reveal a lateral distance of 6.0Â±0.5Å between atoms and a step height of 4.8Â±0.5Å between terraces. A related Temperature Programmed Desorption(TPD) study on the same surface concludes that CC l@sub 4@ is adsorbed dissociatively on the Fe@sub 3@O@sub 4@(111) terminated surface and that only Cl atoms remain on the surface when the dosed surface is flashed up to 590K. STM images after dosing and flashing up to 590K show bright features on the Fe @sub 3@O@sub 4@(111) terminated surface that are identified as individual Cl atoms. These atoms are bound atop Fe atoms, which occupy tetrahedral Fe sites on the Fe@sub 3@O@sub 4@(111) surface, located in three-fold hollow sites of the underlying close-pa cked O plane. STM images before dosing and the chemical reactivity of a Fe@sub 3@O@sub 4@(111) terminated surface with Cl atoms suggest that this Fe@sub 3@O@sub 4@(111) surface is iron-terminated. In contrast, no changes indicating reactivity of the FeO(111) terminated surface were observed. To further clarify the nature of bright features, STM studies are performed where the surface is exposed to Cl@sub 2@ at room temperature.

2:20pm **SS-TuA2 Photo-catalytic Reactions of Organic Molecules Over TiO@sub2@(001) Single Crystal - Effect of Surface Structure***, H. Idriss,* ***J. Wilson***, The University of Auckland, New Zealand

No work has addressed so far the effect of surface reconstruction on the photochemical reactions of wide band-gap oxide semiconductors. Rutile, TiO@sub2@(001) single crystal a n-type semiconductor, band-gap 3.0 eV, is unique in that it possess two stable surface structures that can be obtained by thermal treatment. They are the (011)-faceted (750 K) and the (114)-faceted (> 950 K) surface. We have investigated the steady state reaction of acetic acid (as a prototype organic molecule) under photo-excitation (365 nm) over the two thermodynamically stable surfaces under ultra high vacuum conditions. Acetic acid was readily decomposed at room temperature into CO@sub2@ and CO. Moreover the formation of ethane, by the so-called "Photo-Kolbe" mechanism was clearly observed. On the (011)-faceted and at an acetic pressure of 2.4 x 10@super-7@ Torr the CO@sub2@, CO and, ethane production was 1.02 x 10@super-8@, 1.7 x

10@super-8@, and 4.51 x 10@super-9@ Torr, respectively. The product distribution on the (114)-faceted surface was found similar. However, it appears that this latter surface, the one containing Ti@super4+@ cations in 4, 5 and 6-fold coordination to oxygen anions is less active than the (011)faceted surface (all Ti@super4+@ cations are 5-fold coordinated to oxygen anions), under similar conditions.

2:40pm **SS-TuA3 Semiconductor Photocatalysis over Titanium Dioxide***,* ***D.F. Ollis,*** North Carolina State University **INVITED**

Near-UV illuminated titania surfaces allow for total oxidation of trace organic contaminants in water or air, at room temperatures and with molecular oxygen as the ultimate oxygen source. We examine the origins, progress, and prospects for photocatalysis in four key areas: air purification and remediation, air sterilization, self-cleaning surfaces, and photo-initiated polymeric coatings.

3:20pm **SS-TuA5 Valence Band Photoemission from Pure and Sr Diffused Single Crystal Anatase TiO@sub 2@(001) Surfaces***,* ***S. Thevuthasan****, V. Shutthanandan, M.A. Henderson, G.S. Herman, S.A. Chambers, Y. Liang, C.H.F. Peden,* Pacific Northwest National Laboratory*; S. Mun, N.M. Hamdan, D. Shuh, C.S. Fadley,* Lawrence Berkeley National Laboratory

Single crystal rutile titanium dioxide has been extensively studied as a model oxide surface because of its commercial availability and its wide use in a variety of technological applications. In contrast, investigations of high-quality anatase titanium dioxide are limited in the literature due primarily to the lack of availability of single crystals. Recently, we have successfully grown epitaxial single crystal anatase TiO@sub 2@(001) thin films with high quality surfaces on SrTiO@sub 3@(001) substrates at the Environmental Molecular Sciences Laboratory's (EMSL) MBE facility.@footnote 1@ We have carried out valence band photoemission experiments on pure anatase TiO@sub 2@(001) thin films, and those with outdiffused Sr at the Advanced Light Source. During these experiments, we investigated the valence band region that includes the band gap and O 2p band as a function of photon energy ranging from 35 eV to 80 eV. The results were compared with those for rutile TiO@sub 2@ surfaces. Valence band spectra from sputtered and annealed (in vacuum and oxygen environments) anatase show differences compared to the valence band spectra from rutile surfaces. However, outdiffused Sr results in no visible changes to the valence band spectra. This result suggests that Sr may occupy the cation sites in a strontium titanate-like structure that exhibiting the band gap similar to the band gap of anatase titanium oxide. These results will be discussed along with the ion channeling measurements of Sr outdiffusion and substitution for cation sites. @FootnoteText@ @foontote 1@G.S. Herman, M.R. Sievers, Y. Gao, Phys. Rev. Lett. 84, 3354 (2000). Work supported by the U.S. Department of Energy, Offices of Basic Energy Sciences and Biological and Environmental Research, the Environmental Management Science Program, and the laboratory directed research and development (LDRD) program.

3:40pm **SS-TuA6 Surface Investigations of TiO@sub 2@ Anatase (101)***,* ***N. Ruzycki****, D.L. Ederer,* Tulane University*; G.S. Herman, M.A. Henderson,* Pacific Northwest National Laboratory*; U. Diebold,* Tulane University

Titanium dioxide exists in three cyrstallographic structures, rutile, anatase, and brookite. The surfaces of rutile, especially the most stable (110) face, are very well investigated, but far less is know about the technologically much more relevant anatase phase. We report a study of the lowest-energy face, the (101) surface of an anatase mineral sample. After sputtering and annealing to a temperature of 650°C, a sharp (1x1)LEED pattern is observed. In STM the surface morphology is dominated by small triangularly-shaped terraces separated by monoatomic steps.@footnote 1@ The step directions are consistent with the ones expected from simple bond-counting rules. Surprisingly, very few point defects are observed with atomic-resolution STM images and HREELS. This is consistent with the low surface free energy predicted in first-principles calculations.@footnote 2@ It is in contrast to rutile (110), however, where a similar surface treatment creates a few percent of oxygen vacancies. These surface defects play a major role in the surface chemistry of rutile (110), for example, they promote the dissociation of water.@footnote 2@ Adsorption of water is used to probe the surface reactivity of anatase (101). Predominantly molecular adsorption is found, consistent with the picture that po int defects do not play a major role. @FootnoteText@@footnote 1@W. Hebenstreit, N. Ruzycki, G. S. Herman, and U. Diebold, Phys. Rev. B 64 (24) (2000) R16334. @footnote 2@A. Vittadini, A. Selloni, and M. Gratzel, Phys.Rev.Lett.. 81 (14) 2954. 3. M. A. Henderson, Surf. Sci. 335 (1996) 151.

4:00pm **SS-TuA7 Characterization of Surface Defects on Flat and Porous MgO Surfaces***,* ***Z. Dohnálek****, D. McCready, J.S. Young, A. Dohnálková, G.A. Kimmel, R.S. Smith, B.D. Kay,* Pacific Northwest National Laboratory

We use the physisorption of gases such as N@sub 2@, Ar, and CO and standard surface analytical techniques to characterize the surface defects on thin films of dense and porous MgO. Different types of defects are prepared on the MgO films by careful adjustment of the deposition conditions. Significant changes are observed on the surfaces of films grown on the Mo(100) substrate at various substrate temperatures, O@sub 2@ pressures, deposition rates, and film thicknesses. Temperature programmed desorption (TPD) of physisorbed molecules reveals distinct desorption features associated with different binding sites on the defective films. The analysis of TPD spectra yields the binding energies and concentrations of these defect sites. The information from flat MgO(100) surfaces is utilized in the characterization of porous, crystalline MgO films. Details of the experimental techniques, results, and implications of the results will be presented. @FootnoteText@ Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

4:20pm **SS-TuA8 A Study of the Surface Reconstruction of Fe@sub 3@O@sub 4@ (100) Using Antiferromagnetic Tips***,* ***G. Mariotto****, S. Murphy, I. Shvets,* Trinity College Dublin, Ireland

We have studied the surface structure and chemical composition of an artificially grown single crystal of Fe@sub 3@O@sub 4@ (100) using scanning tunnelling microscopy (STM), low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). The crystal has been also characterized by electrical resistivity measurements as a function of temperature. Two different preparation procedures are discussed. The first one consists of mechanically polishing the sample with diamond paste and then annealing it in situ at a temperature of 990 ± 50 K. It has been found that this procedure gives rise to a surface characterized by the presence of square terraces with the edges aligned along the [110] and [1-10] directions. A p(1x1) LEED pattern has been associated with this type of images and sample preparation. The steps separating adjacent terraces are 2 ± 0.2 Å high, which corresponds to the distance between like sites of iron atoms. A longer annealing induced the onset of a different type of structure: the square terraces split into rows that become sharper and narrower as the annealing time is increased. The separation between these rows ranges from 24 to 40 Å. This type of surface structures manifests itself in the LEED pattern with the presence of satellite spots around the primary spots. Surface contamination by impurities segregating from the bulk are discussed. The second preparation procedure consists of argon ion etching followed by annealing. This method produces a c(2x2) reconstruction that is clearly visible in the LEED pattern. AES spectra indicate a clean surface of magnetite. Terraces separated by 2 ± 0.2 Å are routinely observed. Atomically resolved pictures have been obtained on a sample prepared according to this procedure using an antiferromagnetic MnNi tip. The differences between the two preparation procedures are discussed.

4:40pm **SS-TuA9 Characterization of Copper Oxides Formed by Thermal and Plasma Oxidation Using Linear Sweep Voltammetry, Galvanostatic Reduction and XPS***,* ***M.A. Hossain****,* Lamar University*; J.R. Parga,* Instituto Tec. de Saltillo*; H. McWhinney,* Prairie View A&M University*; R. Schennach,* Technical University of Graz*; D.L. Cocke,* Lamar University

The growing importance of copper in the semiconductor industry has led to a renewed interest in the properties and growth modes of copper oxides under a variety of conditions. While thermal oxidation of copper has been studied extensively over the last decades, recent surface studies seem to ignore the possible formation of Cu@sub 3@O@sub 2@. It has been shown that thermal oxidation of copper leads to multilayer structures, which consist of Cu@sub x@O, Cu@sub 2@O, Cu@sub 3@O@sub 2@ and CuO, depending on the oxidation conditions. These oxides have been analyzed by electrochemical methods, which probe the buried interfaces in an electrical potential controlled order. XPS combined with depth profiling has been used to obtain information which applied with controlled growth complements the electrochemical methods. Linear sweep voltammetry (LSV) and galvanostatic reduction (GR) have been used to characterize the oxides formed by thermal and plasma oxidation. LSV and GR show that plasma oxidation at room temperature leads to the formation of a pure CuO film, which cannot be formed using thermal oxidation and provides insight into the formation of the other oxides and about their subsurface interfaces.

5:00pm **SS-TuA10 The Surface Kinetics of the Initial Stages of Metal Oxidation Visualized by In situ UHV-TEM*, J.C. Yang*,** *G.W. Zhou, M.D. Bharadwaj, D. Evans,* University of Pittsburgh

Copper has played a significant role in the development of oxidation theories, ranging from the classic oxidation studies of the epitaxial growth of the thermodynamically stable oxide scale to the surface science investigations of the dynamics of oxygen interaction with the bare metal surface. We are visualizing the initial oxidation stage of Cu thin films by in situ ultra-high vacuum (UHV) transmission electron microscopy (TEM) where we have varied temperature, oxidation pressures and oxidizing environment. In situ UHV-TEM provides unique information, such as real-time structural changes and information on buried interfaces, where extremely clean surface conditions are obtained inside the microscope. Based on our data, we have developed a semi-quantitative model of the initial oxidation stage where the dominant mechanism for transport, nucleation and growth of oxide islands is oxygen surface diffusion. We are presently examining other metallic systems, such as Aluminum.

Thin Films

Room 123 - Session TF-TuA

Growth and Properties of Thin Films

Moderator: P. Barna, Hungarian Academy of Sciences

2:00pm **TF-TuA1 Mechanical Properties and Stresses in Ion-Assisted Thin Films*, G.S. Was*,** University of Michigan **INVITED**

Understanding the origin of stresses in thin films is critical to the control of film properties. Experiments were conducted to determine the origin of residual stresses in amorphous Al@sub2@O@sub3@ and crystalline Al and Nb films, and to control the stre sses in multilayer structures using ion-assisted deposition. Monolithic films were deposited during bombardment by Ne, Ar or Kr ions over a narrow range of energies, E, and a wide range of ion-to-atom arrival rate ratio, R. Films were characterized in terms of composition, thickness, density, crystallinity, microstructure, hardness and residual stress. Stress varied strongly with ion beam parameters, and with the resulting gas content. Residual stress and gas content saturated at a normalized energy of ~20 eV/atom or an R of ~0.05. Where residual stress varied linearly with RE@super1/2@, results are consistent with an atom peening model, but saturation at high R or RE@super1/2@ is inconsistent with such a model. The various mechanisms for residual stress control in monolithic amorphous and crystalline solids and the application of residual stress control to multilayered structures will be discussed. In Nb and Al films, the mechanisms for controlling crystallographic texture and the application of texture control for improved film properties are also presented. In both systems, texture developed slowly, but produced remarkable effects on plastic flow in the film. Specifically, examples will focus on crystallographic texture control in order to control the strength of the film/substrate interface and susceptibility to plastic flow in the film.

2:40pm **TF-TuA3 Growth of Highly-Oriented CeO@sub 2@ Layers on Glass Substrates for High-Quality Poly-Si Overlayer Formation*, N. Sakamoto*,** *T. Inoue, T. Suzuki, S. Shida,* Iwaki Meisei University, Japan*; K. Kato,* Fukushima Technology Centre, Japan

In order to realize high-performance thin-film transistors, tremendous efforts have been made for growth of high quality polycrystalline Si (poly-Si) films on glass substrates. CeO@sub 2@ films on glass substrates have a potential advantage in attaining high-quality poly-Si overlayers without supplementary crystallization processes such as solid phase crystallization, excimer laser annealing and metal induced lateral crystallization. Systematic experiments varying growth temperature (room temperature 750°C) reveal that orientation controlled CeO@sub 2@ layers can be obtained. CeO@sub 2@ layers with strong (111)-tendency grow in low temperature region, whereas those with (100)-orientation grow at higher temperatures. Comparing conventional evaporation and electron-beam-assisted evaporation,@footnote 1@ the latter gives grain size enlargement and crystallization enhancement. For the films grown by electron-beam-assisted evaporation, the grain size estimated from the full width at half maximum of XRD peaks is 1.1-1.4 times larger than those grown by conventional evaporation. It is verified that poly-Si films with strong (111)-orientation are successfully formed on CeO@sub 2@/glass structures grown at room temperature. @FootnoteText@ @footnote 1@ T. Inoue, Y. Yamamoto, and M. Satoh, J. Vac. Sci. Technol. A, Vol. 19, Jan/Feb (2001) 275.

3:20pm **TF-TuA5 Thin Film Growth of Reactive Sputter Deposited Tungsten-Carbon Thin Films***, P.D. Rack,* Rochester Institute of Technology*;* ***J.J. Peterson****, J. Li,* Advanced Vision Technologies*; H.J. Rack, A.C. Geiculescu,* Clemson University

Tungsten-carbon thin films have been reactively sputter deposited in various Ar-CH gas mixtures and the growth kinetics of the reactive deposition process have been elucidated. X-ray diffraction data reveal that the films are amorphous as-deposited with partial crystallization of W2C and WC occurring following a 1100oC-1 minute rapid thermal anneal. Peak shape analysis of the W and C x-ray photoelectron peaks show binding energy shifts consistent with carbide formation for the annealed films. Carbon incorporation within the W-C films is attributed to flux of CH3 radicals impinging on the growth surface. Although the CH3 radicals have a significantly lower concentration (~0.1%) than the CH4 molecules contained within the plasma, the sticking coefficient of CH3 is significantly larger than that of CH4. In addition, the change in the incorporation rate of carbon in the W-C films at higher CH4 (and subsequently CH3) concentrations has been shown to be due to the changes in the growth surface; as the CH3 flux increases, the growth surface becomes carbon terminated decreases the incorporation of carbon because of the low CH3-C sticking coefficient. This presentation will demonstrate the experimental procedure used in growing the W-C thin films. Compositional analysis as a function of the CH4 concentration will be presented and the growth process will be shown to follow Langmuir-type growth.

3:40pm **TF-TuA6 Reactive Sputter Deposition of Tungsten Nitride Thin Films*, C. Baker*,** *S.I. Shah,* University of Delaware

Tungsten nitride (WN@sub x@) thin films were deposited by reactive sputtering in an Ar/N@sub 2@ atmosphere. The partial pressure of nitrogen in the sputtering gas was varied from 2-50% and the effect of the N@sub 2@ concentration variation on the film properties was investigated. Through examination of cathode current and voltage during the film growth, it is determined that cathode poisoning occurs when the nitrogen concentration in the chamber is increased above 2-5%. This poisoning reduces the film growth rate. Films were characterized by X-ray Photoelectron Spectroscopy. XPS analyses show that the films are composed of ~30% nitrogen when the nitrogen concentration in the chamber is greater than 10%. X-ray diffraction analyses confirm that the predominant phase in the reactively sputtered films is W@sub 2@N, with the characteristic (111) peak found near 2@theta@=37.7Â°. Slight shifts in this peak position are thought to be the result of nitrogen incorporation in interstitial positions, thus distorting the lattice. A post-deposition anneal was carried out which shifted the peak back to its characteristic position confirming that the extra nitrogen was indeed accommodated as interstitial.

4:00pm **TF-TuA7 The Impact of Residual By-Products from Tungsten Film Deposition on Process Integration due to Non-Uniformity of the Tungsten Film*, A. Sidhwa*,** STMicroelectronics, Inc. and University of Arkansas*; C. Spinner, T. Gandy, S. Melosky,* STMicroelectronics, Inc.*; W. Brown, S. Ang, H. Naseem, R. Ulrich,* University of Arkansas

The effects of residual by-products from a tungsten film deposition process and their impact on process integration due to the non-uniformity of the tungsten film were investigated in this work. The tungsten film deposition process involves three steps: nucleation, stabilization, and tungsten bulk fill. Six experiments were conducted in search for a solution to the problem. The resulting data suggest that excess nitrogen left in the chamber following the tungsten nucleation step, along with residual by-products, causes a shift in the tungsten film uniformity during the tungsten bulk fill process. Data reveal that, due to the residual by-products, an abnormal grain growth occurs causing a variation in the tungsten thickness across the wafer during the bulk fill step. Although several possible solutions were revealed by the experiments, potential integration problems limited the acceptable solutions to one. The solution chosen was the introduction of a 10 second pumpdown immediately following the nucleation step. This choice did not create any integration problems as confirmed by subsequent studies.

4:20pm **TF-TuA8 Thermal Stability of Arc Evaporated Ti@sub 1-x@Al@sub x@N Thin Films*, A. Hörling*,** *L. Hultman, M. Odén,* Linköping University, Sweden*; G. Ramanath,* Rensselaer Polytechnic Institute*; P.H. Mayrhofer, C. Mitterer,* University of Leoben, Austria*; J. Sjölén, L. Karlsson,* Seco Tools, Sweden

The thermal stability of Ti@sub 1-x@Al@sub x@N thin films deposited by arc evaporation from cathodes with nominal composition x=0.67 onto substrates kept at 500°C has been investigated by XRD and TEM, and by differential scanning calorimetry (DSC) and 4-point probe measurements. As-deposited films contained 62 at.% Al and were of cubic [NaCl]-structure phase. Annealing of such metastable films results in relaxation of intrinsic compressive stress, together with spinodal decomposition into cubic TiN and AlN-rich phases succeeded by the precipitation of hexagonal AlN. Stress relaxation was observed to take place for all annealing temperatures above the deposition temperature, which implies that point defects or defect complexes become annihilated. For example, DSC showed enthalpy changes at temperatures up to 700°C, and XRD showed a decrease in peak broadening at temperatures up to 800°C. By XRD, the spinodal decomposition stage was revealed as a symmetrical broadening of the cubic (Ti,Al)N (200) peak after annealing at 900°C; by DSC as an exothermic peak starting at 850°C for a heating rate of 27°C min@super -1@; and by 4-point probe measurements as an increased sheet resistance at 500°C with a maximum at 650°C for a heating rate of 5°C min@super -1@. At higher temperatures, the resistivity decreased, and upon cooling and re-annealing showed a reversible behaviour which indicates a parallel-circuit behaviour of a more TiN-like matrix together with emerging AlN phases. Following spinodal decomposition, phase separation of the structure into c-TiN and h-AlN occurred in the temperature range of 900°C-1100°C, being observed by XRD and TEM. The 4-point probe measurements, especially when compared to XRD, indicate that the heating rate has a large effect on the kinetics of phase separation. This observation will be discussed, together with results of activation energies for the various reactions.

4:40pm **TF-TuA9 Evolution of Ti-3Al Film Structures and its Effect on Film Properties*, C.-F. Lo*,** *D. Draper, P. McDonald, P. Gilman,* Praxair-MRC

The evolution of Ti-Alx film structure deposited from the Ti-75at%Al (Ti-3Al) sputter targets was investigated. 300nm, 900nm and 9000nm thick films were deposited on three inch diameter silicon wafers at various wafer temperatures from 20°C to 400°C. The films were evaluated for composition, microstructure, crystallinity, hardness and elastic modulus using the FE-SEM, XRD and nano-indentation instrument. In order to understand the effect of the target structure on film properties, the target manufacturing process for the Ti-75 at%Al (Ti-3Al) alloy system was controlled to prepared two four inch diameter targets, one metallic (Ti+3Al) and one intermetallic (TiAl@sub 3@) structures. No effect of target structure and sputtering conditions on the composition of the deposited films was observed. The film compositions were similar to that of the sputtered targets. At a film thickness 300nm and less, the grains showed an equiaxial shape with size about 40nm. The columnar grains generated and grew with increasing of film thickness. The diameter of the columnar grains increased with increasing of film thickness. The target structure showed some effect on the morphology but not on the diameter of columnar grains. XRD analysis showed that TiAl was the major phase existing in all the tested films. The hardness and elastic modulus measurements showed that the mechanical properties of the deposited films were effected by the film microstructure.

5:00pm **TF-TuA10 Surface Structural Anisotropy in Sputter and Electrolytic Deposited Tantalum Films*, S.L. Lee,*** US Army Armament Research Development and Engineering Center*; D. Windover,* Rensselaer Polytechnic Institute

We studied the growth surface texture of tantalum films generated by sputter and electrolytic deposition processes for high temperature and pressure wear and erosion applications, using conventional and image plate XRD. Electrochemically deposited bcc tantalum coating in eutectic molten salt solution at 800°C on 20mm-diameter 4340 steel cylinder revealed near random grain orientation. Triode sputtered tantalum deposition on steel generally showed weak anisotropy. Example specimens deposited in krypton gas at 200°C-250°C revealed (110) and (211) texture with poles. Planar magnetron sputtered tantalum film on a steel plate with a thin electrolytic chromium interface layer produced bcc tantalum film with (111) fiber texture, following the (111) fiber texture in chromium. Planar magnetron sputter-deposited 200nm film on a (100) silicon wafer, mixed bcc and tetragonal tantalum and (110) fiber texture with azimuth symmetry evolved. Random oriented grain distribution suggests uniform thermal-mechanical properties in polycrystalline solids. Model calculations of Young's modulus and Poisson's ratio for isotropic tantalum crystalline aggregates were made. Evaluation of directional modulus, e.g., E110, E100, E111, from single crystal elastic constants, suggested higher elastic modulus in the out-of-plane direction for (111) fiber-textured films.

Vacuum Science & Technology
Room 125 - Session VST-TuA

Vacuum Gas Dynamics

Moderator: J.C. Helmer, AVS Fellow

2:00pm **VST-TuA1 Calculated Energy Transfer in an Accommodation Pump*, J.P. Hobson*,** National Vacuum Technologies Inc., Canada

In an accommodation pump gas is transferred from one point to another at the same temperature without the application of any external mechanical or electrical forces to the gas - only temperature gradients are used.@footnote1@ If there is no continuous gas flow a static and unchanging pressure difference develops between the two points, requiring no additional input of energy. Little attention has been paid to the energy transfer, i.e. the number of calories per mole of gas pumped, in this process. A simple model is presented in which this energy transfer is analytically calculated for a single-stage Pyrex accommodation pump,upper temperature room (295 K), lower temperature liquid nitrogen (77.4 K), with gas helium, compression ratio 1.2, and pressure in the free molecular range. Under these conditions the physical adsorption of helium on pump surfaces is quantitatively negligible. The model calculates the energy differences between a true accommodation pump with smooth and rough (leached) surfaces and a non-pump of exactly the same geometrical dimensions, but with all surfaces rough. The energy differences are assigned to accommodation pumping. It is found that an energy in the range of 150 calories per mole, is required, independent of the overall size of the pump, but becoming smaller as the cold volume is decreased relative to the warm volume. The results are extended to multi-stage pumps, which are ponderous to calculate analytically, but which bear a simple relationship to a single-stage pump. @FootnoteText@ @footnote1@ J.P.Hobson and D.B.Salzman, J. Vac. Sci. Technol. A 18(4), 1758-1765, 2000

2:20pm **VST-TuA2 Rapid Modelling of Molecular Flow in Steady-State Arbitrary Geometries*, M.A. Galtry*,** *R.G. Livesey,* BOC Edwards, UK*; A. Ghobadian,* Computational Dynamics Ltd.

Analysis of molecular flow in simple geometries is commonly approached using methods such as Monte Carlo or view factor analysis. These methods are applicable to a generalised geometry but require significant rework for even small geometry changes, rendering them impractical for rapid engineering design analysis. A method is developed, drawing on the strong analogy between Knudsen cosine reflection for molecules and Lambert diffuse reflection for radiation, where analysis is conducted using the heat transfer facilities of a commercial code. Test cases establish the accuracy of the method, and practical examples illustrate its use in arbitrary topologies.

4:20pm **VST-TuA8 Edison's Vacuum Technology Patents*, R.K. Waits,*** Consultant

In 1879 Edison's laboratory had developed the means to evacuate glass lamp globes to less than a mTorr in twenty minutes.@footnote 1@ Among Edison's nearly 1100 patents are five for vacuum pump improvements and at least nine others that are vacuum-related; most were applied for in 1880-1881. Edison had hired Ludwig Boehm, who had worked for Geissler, to construct Geissler pumps and "mercury drop" pumps based on those developed by Crookes and Sprengler and used in experiments described by de la Rue and Muller (France) in 1878. The Sprengler pump required a continuous gravity-fed stream of mercury droplets to trap, compress, and exhaust the air. Edison patents describe means to automate the delivery of the mercury. Other patents described the vacuum technology that Edison investigated and employed. Various means were used to remove residual gases: driving adsorbed water from glass by direct heating, and using iron particles or incandescent iron "to decompose moisture," phosphorous pentoxide and charcoal to absorb moisture, halogen or a halide to remove mercury vapor, metals such as copper or zinc to remove chlorine, and "magnesia, charcoal, and other inert substances which absorb gases in their pores." Pressure was measured with a McLeod gauge, and a high (hard) vacuum was indicated when the glow discharge in a Geissler tube was extinguished. Edison also patented a method for preserving food by sealing in an evacuated glass globe (but omitted the essential bacteria-killing heating step). A vacuum was also required for the evaporation and sputter-coating processes that later were used to produce molds for the manufacture of phonograph cylinders.@footnote 2@ @FootnoteText@ @footnote 1@R. Friedel, P. Israel and B.S. Flinn, "Edison's Electric Light: Biography of an Invention," Rutgers Univ. Press (1987), pp. 61-62. @footnote 2@ R.K. Waits, J. Vac. Sci. Technol. A 19(4), Jul/Aug 2001.

Applied Surface Analysis
Room 134/135 - Session AS-TuP
Aspects of Applied Surface Analysis II Poster Session

AS-TuP1 XPS and XAES Characterisation of the Interaction of Copper-containing Alloys with Ultra-pure Water in Oxidising and Reducing Conditions*, J.E. Castle,* ***P.A. Zhdan,*** University of Surrey, U.K.

X-ray photoelectron spectroscopy (XPS) and X-ray Auger electron spectroscopy (XAES) were used to characterise changes in the surface chemistry of different copper alloys (admiralty brass, Al brass and 90Cu-10Ni alloy) as a result of their interaction with ultra-pure water at 95C for periods of up to 200 hours. All alloys were treated at pH 8-11.5 using oxygen-containing water (oxidising environment) and oxygen free water (reducing environment). This allowed us to determine the role of the dissolved oxygen in changes of the chemistry of the resulting surface products. The surface composition of representative samples before and after treatment was determined by XPS and XAES using the ESCALAB 2 and the SigmaProbe electron spectrometer (VG Scientific, UK) with monochromatised Al radiation. Experimental results for admiralty brass demonstrated that under reducing conditions the protective surface layer is cuprous oxide while under oxidising conditions the surface oxide contains increasing amounts of cupric oxide (CuO). When a reducing condition is changed to an oxidising condition at an operating temperature of 95C with pH 9 - the surface layer undergoes a conversion from cuprous to cupric oxide. After exposure of admiralty brass at pH 10.5 the surface is mainly composed of zinc oxide and no cupric oxide was present on the surface after its exposure to an oxidising environment at pH 11.5. The role of the alloy composition to chemistry and stability of resulting surface products is discussed and the marked effect of the addition of carbon dioxide on the composition of surface layers formed in oxidising conditions is demonstrated.

AS-TuP2 Non-destructive Depth Profiling Analysis of @beta@-FeSi@sub2@ Formation Process by SR-XPS*,* ***T. Saito,*** Japan Atomic Energy Research Institute, JAPAN*; H. Yamamoto,* Japan Atomic Energy Research Institute, Japan*; H. Asaoka, K. Hojou,* Japan Atomic Energy Research Institute*; M. Imamura, N. Matsubayashi, H. Shimada,* National Institute of Advanced Industrial Science and Technology, Japan

In recent year, semiconducting iron silicide,@beta@-FeSi@sub2@ is extensively attracted because of its semiconducting character. In the present study, the formation processes of @beta@-FeSi@sub2@ during solid-phase epitaxy (SPE) from Fe thin films on Si (111) surface have been investigated by means of X-ray photoelectron spectroscopy using synchrotron radiation (SR-XPS). All the experiments were carried out at a soft X-ray beam line (BL-13C) of Photon Factory. Non destructive depth-profiling analysis with changing excitation energy (220 - 900 eV) revealed that the surface composition of the iron deposited substrate was gradually changed with rising annealing temperature indicating aggregation or diffusion of the surface iron. The comparisons of experimental results with simulation results using inelastic mean free path (IMFP) of electron in Si and Fe revealed that the surface iron was diffused into Si bulk gradually with rising annealing temperature. The changes in the core-level Fe 2p photoemission spectra indicated the formation of iron silicide above annealing temperature of 673K. The valence-band photoemission spectra also indicated that metallic surface iron changed into semiconducting @beta@-FeSi@sub2@ phase by the annealing. These diffusion and silicide formation behavior were influenced by the thickness of the initial iron layer before annealing suggesting the importance of the iron diffusion in @beta@-FeSi@sub2@ formation process.

AS-TuP3 X-ray Photoelectron Spectroscopy and Auger Electron Spectroscopy Studies of the Effect of a Pre-oxidation Clean on Boron And Residual Fluorine Distributions in Ultra-shallow Junction BF2+ Implants*,* ***E.G. Garza,*** *S.N. Raman,* Advanced Micro Devices

The distribution of as-implanted boron and fluorine in ultra-shallow junction 49BF2+ implants was investigated using X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). The effects of a pre-oxidation clean following low energy, high-dose 49BF2+ implants (LEHD) were also investigated. Auger and XPS depth profiles and angle-resolved XPS (ARXPS) studies reveal significant dopant retention in the native oxide and subsequent high degrees of dopant loss due to removal of the native oxide during a standard SPM/APM/HPM clean process. Fluorine Auger parameter analysis was also performed to identify changes in fluorine binding states.

AS-TuP4 X-ray Photoelectron Spectroscopy Study of As-implanted and Annealed Ultra Shallow Junction 75As+ Implants*,* ***S.N. Raman,*** *E.G. Garza,* Advanced Micro Devices

Implant depth and silicon binding states in as-implanted and annealed ultra-shallow junction 75As+ implants were characterized using X-ray photoelectron spectroscopy (XPS). Dopant profiles were merged with secondary ion mass spectrometry (SIMS) depth profiles to complete the dopant distribution in the initial transient region. Doped regions of the implanted silicon substrate were identified using shifts in the Si2p photoelectron energy. The effects of rapid thermal annealing on Si2p energy are also presented.

AS-TuP5 The Particularities of In-line Control Tools Employing Electron Spectroscopic Methods*,* ***L. Vasilyev,*** *C. Bryson, D. Klyachko, B. Linder,* Surface Interface Inc.

The minitiaturization of electronic devices will inevitably lead to the development of the new methods of in-line control. One of the good candidates for such a method of in-line control is electron spectroscopy that is characterized by a better surface sensitivity compared to the currently used optical methods. In addition, electron spectroscopy provides quantitative information regarding the chemical composition of thin films at the surface. The specific requirements to the in-line control tools affect the design of electron spectrometers now mostly used in the research laboratory environment. 1. The in-line tool is application specific. It is optimized to perform a limited number of tasks with a best possible reproducibility and a required precision. 2. The tool must be simple in use and can be operated by a technician with a rather low education level. This requires high degree of automation that includes control of the system status, in-line data analysis and data reduction, aiming to detect and eliminate wrong data, quantify the results and perform self-diagnostics and calibration. 3. The software is an integral part of the tool that is specific for a given type of the hardware. By limiting its flexibility it is possible to reduce the time and cost of its development and to customize for a particular task. 4. High throughput and low price are the key issues for the in-line tool to be accepted in industry. Non-traditional and application specific design of the vacuum chamber and the measurement units could substantially reduce their price and increase the throughput. 5. The whole power of the electron spectroscopy (not only AES and XPS) must be utilized for these applications. For example, Beta backscattering can be utilized for film thickness control in hard drive industry. Here we describe our experience of the development of in line control electron spectrometer utilized for thin carbon based overcoat control.

AS-TuP6 High Spatial Resolution Auger Microanalysis of FIB Prepared Samples*,* ***A.L. Linsebigler,*** *M. Larsen,* General Electric Corporate Research and Development Center

In the past several years, the realm of Auger microanalysis has been expanded to include analysis of nanometer range thin films and particles. Auger analysis is ideal for fast and simple elemental determination of thin film and particle composition on a submicron level. In most cases, the area of interest is buried below the surface of the sample out of the range of the Auger electron sampling depth. Traditional metallographic sample preparation techniques can be used to prepare a cross section of a sample to expose buried layers and particles. The surfaces of samples can also be polished to produce high spatial resolution (< 0.3um) Auger elemental maps. Traditional metallographic polishing techniques require that the sample be mounted in nonconductive materials and require the use of liquid polishing media, which can absorb into microcracks in the mounting material and sample. This in turn, leads to considerable outgassing under the ultrahigh vacuum conditions needed for Auger analysis. In addition, the traditional techniques can miss the submicron area of interest, take a considerable amount of time, and lead to smearing and rounding of interfaces. FIB sample techniques are UHV compatible, are well controlled to prepare the submicron area of interest, and certain FIB sample preparation methods are much faster than traditional polishing methods. Auger microanalysis of a cross-sectional surface of buried submicron thin films prepared with the box, staircase, and TEM lift out FIB techniques will be presented and the results will be compared to the same surfaces prepared by traditional metallographic polishing techniques. A comparison between the Auger interfacial resolution, surface roughness, and surface cleanliness obtained with each technique will be presented.

AS-TuP7 Applications of AFM/SCM in Process Control and Failure Analysis of Semiconductor Devices*, **K.-J. Chao**, J.R. Kingsley, H. Ho, H. Shen, I.D. Ward,* Charles Evans & Associates

As the minimum feature size of a semiconductor device continues to shrink, analyses of the engineered structures and materials of semiconductor devices have been very critical in device manufacturing and the development of new generation devices. Furthermore, the performance of a modern device is strongly influenced by its dopant distributions in depth and laterally. Scanning capacitance microscopy (SCM) is one of the techniques that have been developed to reveal the dopant distribution two-dimensionally. In this work, AFM/SCM was applied to both process control and failure analysis of semiconductor devices. Two types of semiconductor devices, Si based and GaAs based, were studied. In the applications of process control, two examples are presented. The first example is to investigate the uniformity of the As layer of a silicon substrate. This sample has a layer of uniformly distributed As region. X-sectioned SCM/AFM study found local non-uniformity in the As layer. The second example is to determine the lateral diffusion length of dopants after the thermal annealing process. A GaAs substrate is masked and patterned by a layer of Si3N4. Zn dopants were thermally dif-fused through a line-opening in the Si3N4 layer into the GaAs substrate. By overlaying the AFM image on top of the SCM image, the lateral diffusion length of the Zn dopants was found to be about 2.2Âµm away from the edges of the exposed GaAs region. Another important application of AFM/SCM is in the device failure analysis. A failed p-channel transistor was first studied by AFM/SCM. Two levels of dopant concentration were found in the corresponding source and drain regions by SCM. Another way to identify the cause of the failure is to directly compare the failed device with a properly functioning one. We applied AFM/SCM to study the same N-well struc-tures in two devices, one good and the other failed, and found that the depth of the N-well for the failed device is about 0.4Âµm shorter.

AS-TuP8 Surface Analysis of Shock-compacted Nd-system Superconductor*, **H. Kezuka**,* Tokyo University of Technology, Japan*; M. Kikuchi, K. Fukuoka, E. Ohshima,* Tohoku University, Japan*; S. Yoshizawa,* Meisei University, Japan*; T. Suzuki,* Tokai University, Japan

Shock compaction experiments are performed in vacuum for Nd-system superconductor particles (NdBa2Cu3O7-x) which has a peak effect in the high magnetic field region of near 2T. The as-shocked specimen shows an c-axis oriented crystal structures with the lattice constant of the orthorhombic cell:a=0.5787nm, b=0.5874 and c=1.17462nm calculated by XRD(X-ray powder diffraction method)-analysis just after the shock compaction under 5.7Gpa. From SEM(scanning electron microscopy)- and AFM (atomic force microscopy)-observations, the surface of the specimen for as-shocked Nd-system has larger grains of 4-10 micrometer in length with growth steps caused mainly frictions among the particles in shock compaction.

AS-TuP9 Surface Oxidation of NiTi Shape Memory Alloy*, **R.G. Vitchev**,* Katholieke Universiteit Leuven, Belgium*; G.S. Firstov,* On leave of absence from National Academy of Sciences of Ukraine*; H. Kumar, B. Blanpain, J. Van Humbeeck,* Katholieke Universiteit Leuven, Belgium

NiTi shape memory alloys are often used as materials for medical implants. It is known that the biocompatibility of the implants fabricated from NiTi depends on their surface composition since nickel often causes allergic and toxic reactions. Protective titanium oxide layers on the NiTi surface are often created since they can prevent the contact of Ni with the body tissues. The purpose of this study is to determine the oxidation mechanism of the NiTi alloy. The samples were oxidised in air in the temperature range 473-1073 K. Scanning electron microscopy was used to study the morphology and composition of the oxidised surfaces. The kinetics of oxidation was investigated by means of thermo-gravimetry. X-ray photoelectron spectroscopy and Auger electron spectroscopy combined with sputter depth profiling were used to investigate the surface composition and chemical state of the constituent atoms and their depth distribution. Grazing incidence X-ray diffractometry and Raman spectroscopy were implemented to determine the phases formed in the oxide layers. Thermodynamic calculations were performed to explain the oxidation behaviour of the NiTi alloy.

AS-TuP10 Structure and Corrosion Properties of PVD CrN Coatings*, C. Liu,* Loughborough University, UK*; Q. Bi,* Hull University, UK*; H. Ziegele,* BMW Group, Germany*; A. Leyland, **A. Matthews**,* Hull University, UK

Corrosion of PVD CrN coated steels in an aqueous solution is usually by galvanic attack due to the difference in electro-potentials between the steel substrate and the coating material which causes corrosion activity in through-coating defects (e.g. pinholes). The structure related variables which can determine corrosion performance of CrN coatings include: (i) Surface discontinuities and uniformity of coverage; (ii) Open and through-coating porosity; (iii) Film density and chemical stability; (iv) Growth stresses and associated strain; (v) Interfacial adhesion and the properties of intermediate layers; (vi) Coating thickness; (vii) Substrate properties (e.g. activity and morphology); (viii) Coating composition. In this study, PVD CrN coatings were prepared with different composition, thickness, and surface roughness by changing the nitrogen flow rate, applying multilayering techniques and changing the substrate finish prior to coating, respectively. It has been found that the microstructure of CrN coatings can vary with the N content in the film, thus their corrosion performance can be affected significantly by nitrogen flow rate during coating preparation. The steel substrate surface finish (i.e. roughness) can affect the uniformity and coverage of PVD coatings, as the grooves and inclusions on the original substrate can raise the susceptibility of the coated systems to crevice corrosion. Increased film thickness can greatly reduce the through-coating porosity; this makes the coatings less permeable in terms of solution penetration, such that the corrosion resistance of the system can be enhanced significantly.

AS-TuP11 Analysis of Boron-, Germanium- and Fluorine Diffusion through a SiO@sub 2@ Gate Oxide Into Silicon using Secondary Ion Mass Spectrometry*, **F. Persson**, H. Svensson, U. Södervall, M. Willander,* Chalmers University of Technology, Sweden

This project work is a study of diffusion using in-situ B-doped, B- and BF-implanted samples as sources for boron. The main aim of this report is to see how fast boron and germanium moves through a SiO2 gate oxide into a Si-matrix. To get an answer to this and other questions, we have with a SIMS analyzed annealed specimens at different times and temperatures. Using Fick's law and data from the SIMS, the diffusion constants have been determined. An interesting fact emerging is the dependence of the oxide thickness as a barrier against penetration. SiO2<2,5 nm let through atoms at 950°C and 240 s while SiO2<3 nm is pervious first at 1050°C and 60 s. Another observation is the anomalously high values of boron after the annealing, especially where germanium is involved. Besides, boron penetrates faster from a SiGe gate than from pure Si. The fast influx of fluorine from the BF-implanted samples is also worth mentioning. According to our results, in-situ B-doped gate is preferable to B-implanted gate as gate material. In-situ doping provides a highly uniform profile from surface to the SiO2 interface. By implantation it is difficult to achieve a uniform doping profile, which can lead to gate-depletion or by annealing to an increased boron penetration through the oxide.

Advancing toward Sustainability Topical Conference
Room 134/135 - Session AT-TuP
Poster Session

AT-TuP2 Global Warming Gas Emission During Plasma Cleaning Process of Silicon Nitride PECVD Chamber Using C@sub 4@F@sub 8@O and Mixtures*, **K.J. Kim**, Y.S. Ahn, N.-E. Lee, B.H. Oh, J.H. Kim, G.Y. Yeom,* Sungkyunkwan University, Korea

The emission of perfluorocompounds (PFCs) into the atmosphere has caused growing concern in the semiconductor industry because of their potential global warming effects. PFCs used in plasma cleaning process of CVD chamber are mostly responsible for the global warming. Therefore, the semiconductor industry is proactively seeking ways to reduce PFCs emissions through the use of alternative process chemicals, process optimization, and abatements including destruction and recovery. Among those, the use of alternative gases is expected to be most promising. In this work, C@sub4@F@sub8@O gas was used as an alternative process chemical that has better destruction removal efficiency (DRE) than other alternative gases, such as NF@sub3@, C@sub3@F@sub8@, and C@sub4@F@sub8@. Plasma cleaning of silicon nitride using gas mixtures of C@sub4@F@sub8@O/O@sub2@, C@sub4@F@sub8@O/O@sub2@/Ar, and C@sub4@F@sub8@O/O@sub2@/N@sub2@ was investigated in order to evaluate the effects of adding different gases to C@sub4@F@sub8@O on the global warming effects. First of all, we determined an optimum cleaning condition as processing condition such as additional gases mixture ratio, total gas flow, and working pressure. Under this condition, we quantified the emitted net PFCs while cleaning silicon nitride and then compared the effects of adding different gases to C@sub4@F@sub8@O by evaluating the destruction removal efficiency (DRE) and the million metric tons of carbon equivalent (MMTCE). DRE and MMTCE were calculated by evaluating the volumetric emission using Fourier transform-infrared spectroscopy (FT-IR). DRE values as high as 98% were obtained and MMTCE values were decreased by as high as 90% compared to the case of C@sub2@F@sub6@/O@sub2@. Indirect recombination characteristics were investigated by combining the measurements of species in the chamber using optical emission spectroscopy (OES) and quadrupole mass spectroscopy (QMS), before and after the cleaning processing.

Biomaterials
Room 134/135 - Session BI-TuP
Surface Characterization and Non-Fouling Surfaces Poster Session

BI-TuP2 Short-term Oxidation of Polymer Films Deposited from Pulsed Radiofrequency Allylamine Plasmas*, **J.D. Whittle**, G.R. Kinsel, R.B. Timmons,* University of Texas at Arlington

Plasma deposited films are seen as a promising route to the synthesis of novel functional coatings for a large number of potential applications. Allylamine deposited films in particular are of great interest in the biomaterials field as surfaces for protein adsorption. Studies of the long-term aging of these plasma polymers have shown that the oxygen content of the films changes over extended periods of time. Earlier work has shown that the oxygen content of allylamine films deposited from continuous wave plasmas increased from around 2% for a fresh sample, to around 10% after a year of aging in the laboratory, with the greatest change in composition being within the first 48h. In addition, some loss of nitrogen from the films has also been observed. In this study, we concentrate on the changes in chemistry over the first few days, and in particular the first 12 hours following deposition. The surface chemistry is investigated by X-ray photoelectron spectroscopy (XPS) and Matrix Assisted Laser Desorption/Ionization Mass spectrometry (MALDI-MS). Using XPS we investigate the stability of the plasma polymer surfaces in the UHV environment using different substrates for deposition to determine what the source of the oxidative species may be. A small amount of oxygen is always present in these plasma polymers, which may be due to the unavoidable exposure to the atmosphere between completing the deposition, and insertion of the sample into the spectrometer. Further, by analyzing samples exposed to the laboratory atmosphere for specific lengths of time, we show how the surface chemistry evolves in the first few hours following deposition. We also examine the effect of plasma power and pulsing duty cycle on the post-deposition properties of the films.

BI-TuP3 Fast Impedance Spectroscopy Measurements on Supported Lipid Bilayer Membranes with and without Incorporated Ion Channels*, **G. Wiegand**, S. Beyer, N. Arribas-Layton, P. Wagner,* Zyomyx Inc.

A substantial part of the mammalian proteome is represented by proteins that are either associated or incorporated into lipid bilayer membranes. Our goal is to provide appropriate platform assays and transducer technologies for the functional analysis of membrane proteins. Our special focus is on ion channels due to their pharmacological relevance. Because ionic flux thru an ion channel generates an electrical signal, electronic transducer technologies are the most direct detection method for ion channel analysis. We developed a method of fast impedance spectroscopy that combines the power of a spectroscopic technique providing high information content with the millisecond time resolution of a fast analytical tool. In biophysical experiments, time dependent quantities such as the membrane resistance and the membrane capacity are obtained from the measured sequences of impedance spectra. Supported lipid bilayers provide membrane matrices for protein incorporation that are coupled to solid surfaces. Supported bilayer applications take advantage of the high membrane stability imparted by the solid support, and of the improved accessibility for analytical tools due to the two-dimensional geometry. As a result of the chip compatibility, supported membrane systems are potentially useful in high-throughput technologies. By application of fast impedance spectroscopy, dynamic properties of supported lipid bilayers with and without incorporated ion channels are studied during formation, relaxation and in various states of conduction.

BI-TuP5 Optical Inverted Microscope with a Scanning Near Field Optical Microscope to Study Biological Material*, A. Cricenti, **R. Generosi**, M. Luce, P. Perfetti,* ISM-CNR, Italy

A scanning near field optical microscope (SNOM) has been added to a standard inverted optical microscope with the dedicate aim of characterizing the inner parts of biological molecules. Therefore, in addition to the requirements of reliability and mechanical stability we have carefully looked to analyzing a sample with all available geometries for input/output of photons, in order to get as many information as possible. The SNOM unit consists of a support mounted on the optical microscope arm containing a piezoelectric scanner. The reflectivity of the sample can be measured by applying different methods: the sample can be illuminated on top by an external source, as well as by the optical fiber used for the detection of the reflectivity signal. Absorption experiments can be easily performed by detecting the transmitted signal through the optical apparatus of the inverted microscope.Also fluorescence signal can be simultaneously detected. Reflectivity, transmissivity and fluorescence measurements will be presented on several biological systems, with a resolution well below the diffraction limit.

BI-TuP6 Investigation of Bone Tissues using Infrared Spectroscopic Ellipsometry*, **G.M.W. Kroesen**, J.-C. Cigal, E. Stoffels, B. van Rietbergen, R. Huiskes,* Eindhoven University of Technology, The Netherlands

Small fractures on the bone surface, called micro-cracks, are formed throughout the lifetime as a result of e.g. mechanical stress. In individuals of advanced age, these defects are no longer efficiently repaired by the organism. Increasing density of micro-crack is one of the important factors which lead to osteoporosis: the severe loss of bone mass and attendant fragility of the skeleton. The size of micro-cracks is in the order of 10 microns, and they are difficult to detect in vivo. Apart from these fractures, the chemical composition of the bone surface is expected to change in the course of ageing. Spectroscopic ellipsometry is a powerful but non-destructive technique of analysing complex surfaces, and it seems very suitable in a study of bone tissues. We developed a spectroscopic ellipsometer combined with a Fourier transform spectrometer in the middle infrared range (wavelength of 2.5 to 10 microns). This device allows to collect accurate data on the chemical composition of the bone surface. In addition, it can provide information about the surface roughness, which is useful in determining the density of micro-cracks. Ellipsometry is a purely physical method, and this novel application to the complex biological environment poses many technical challenges. We will present preliminary results on ellipsometric analysis of bone surfaces, including infrared spectra of several bone samples. In the subsequent study we will investigate how the ageing of the bone tissue is reflected by its infrared properties.

BI-TuP7 Changes in Bone Surface after Exposure to an Electric Discharge*, **J.H.R. Feijen**, C.Y.M. Maurice, E. Stoffels, G.M.W. Kroesen, B. van Rietbergen, R. Huiskes,* Eindhoven University of Technology, The Netherlands

Human bones are subject to a continuous process of regeneration. Due to mechanical stress, cracks on a microscopic scale are generated in bone tissue, but in the healthy situation these cracks are repaired before they can lead to serious damage. In the case of disturbed bone regeneration, however, due to osteoporosis, drugs that inhibit bone resorption or bone cancer, the mechanical integrity of bone is impaired by accumulation of micro cracks or large metastatic defects. Treatment of bone diseases in vivo is nowadays very difficult. We consider an alternative method of bone surface processing, using non-equilibrium (cold) electric discharges. These plasmas combine high reactivity with non-destructive character. In this study we attempt plasma treatment and observe its impacts on the surface of bone tissues. These impacts are change in roughness, etching of some layers, removal of cells, etc. Since the concept of exposing living tissues to electric discharges is new, the presented results are preliminary and the medical implications are not yet resolved. For this experiment we employ a low-pressure inductively coupled plasma (ICP), supplied with diagnostics. A Langmuir probe, an energy-resolved mass spectrometer and a Doppler shifted laser-induced fluorescence (DSLIF) techniques are used to monitor the parameters of the plasma. With an Environmental Scanning Electron Microscopy (ESEM) we record images of the surface before and after exposure to the plasma. Several gases will be investigated, like oxygen, hydrogen and argon, and plasma treatment under various conditions (varying pressure, power and electric bias) will be performed. In the continuation of this work, cold atmospheric discharges will be used for bone treatment.

BI-TuP8 Glass Ionomer Cements: Probing Uptake from Solution using Surface Sensitive Techniques*, B.M. Hutton, G. Palmer, P.C. Hadley,* University College London, UK*; T.A. Steele, A.J. Eccles,* Millbrook Instruments Ltd., UK*; R.W. Billington, G.J. Pearson,* Queen Mary, UK*; **F.H. Jones**,* University College London, UK

Glass ionomer cements (GICs) are dental filling materials with the ability to take up ionic species (e.g. F@super -@) from solution and store them within the cement matrix for subsequent re-release. This offers the potential for controlled drug release in-vivo. Previously, ion uptake and release by such materials has been determined primarily by measuring ion concentration in solution.@footnote 1@ Although this approach provides useful data on the concentration of ionic species as a function of time, little is learned about the mechanism of uptake and release. In the current work, X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS) have been used to examine ion uptake. Cements were analysed after the introduction of fluoride either by doping or by immersion in KF(aq) of various concentration. Immersion of a GIC based on poly(acrylic acid) and a calcium aluminosilicate glass was found to result in the formation of a calcium and fluoride rich surface layer, while doping by mixing with KF solution during GIC preparation resulted in no such surface layer. The formation of CaF@sub 2@-like layers on immersion was entirely unexpected on the basis of previous solution-based experiments and may explain differences in measured uptake kinetics. The use of these techniques has been extended to examine the inclusion of molecular active species (amprolium hydrochloride and chlorhexidine acetate) within the GIC matrix. Both species could be detected in GIC samples irrespective of whether they were included by mixing or by immersion in solution. However, relative peak intensities indicated that the binding of the active molecule is dependent on the method of inclusion. Significant applications in the study of the uptake and release mechanisms of active species such as antibacterial and antifungal agents are envisaged. @FootnoteText@ @footnote 1@ Hadley P, Billington RW, Pearson GJ. Biomaterials 1999;20:891-897.

BI-TuP9 Morphological Analysis of the Collagen Structure of Regenerated Rat Tendons Following Laser Photo-stimulation*, **V. Baranauskas**,* Universidade de Campinas - Brazil, Brazil*; N.V. Parizotto,* Universidade Federal de Sao Carlos - Brazil

Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) were used to comparatively study the structure of regenerated rat tendons submitted to laser photo-stimulation after a surgical injury that extracted around 6 mm of Achilles'' tendon (tenectomy) of the left forefoot. The experiment was performed using male Rattus norvegicus albinus, lineage Wistar, with body weights in the range of 250 to 300 g, and 90 days old. The healing course was monitored at 7, 14, 21 or 28 days after the injury. The animals were divided into four groups. One group was used as a control and the other three were subjected to irradiation of doses of 0.5, 5.0 and 50 Jcm-2, respectively. A He-Ne laser of 6 mW power (L = 632.8 nm) was used. AFM and SEM images, at different magnifications, allowed the identification of the time-dependence of the recovery, measured by the organization of the collagen fibers. Comparison of natural recovery processes with the laser photo-stimulation procedures will be discussed.

BI-TuP10 Evolution of a UHV Compatible Heater for TSG Preparation*, M. Hasselblatt, **B. Jackson**, M. Heidecker, P. Wagner,* Zyomyx, Inc.

Template Stripped Gold (TSG) surfaces have been used extensively as a source for ultra-flat substrates. The preparation of these thin gold films relies on accurate temperature control. Heating in UHV / HV is always difficult since an accurate temperature measurement requires excellent thermal contact with the sample due to the lack of convection. Working with layered crystals like mica makes matters worse. Here we present the evolution of an ultra-high vacuum compatible heating plate that is optimized for the preparation of TSG. Initial versions of this heater were successfully built by casting Omegabond 600 High Temperature Chemical Set Cement into a Teflon mold including pre-coiled Omega Nickel Heating Wire and thermocouple wire. The current design features an exceptional degree of thermal homogeneity over approx. 9 square inches with variations of less than 1% and also a modular design to improve serviceability.

BI-TuP11 Imaging Biomolecules for Skin Cancer Demarcation*, **M.B. Ericson**, A. Rosén,* Chalmers University of Technology - Göteborg University, Sweden*; A.-M. Wennberg, C. Sandberg,* Sahlgrenska University Hospital - Göteborg University, Sweden*; F. Gudmundsson,* Chalmers University of Technology - Göteborg University, Sweden*; O. Larkö,* Sahlgrenska University Hospital - Göteborg University, Sweden

Protoporphyrin IX, Pp IX, is a photoactive porphyrin molecule formed in the cell heame synthesis. It has been shown that Pp IX is formed to a larger extent in tumor cells due to enzymatic and metabolic differences compared to normal cells. This effect can be enhanced by exposing the cells to an excess of aminolevulinic acid, ALA, a precursor in the heame synthesis. By imaging the fluorescence from Pp IX molecules in the skin, the extension of skin tumor can be visualised with respect to the enhanced Pp IX production. This technique is based on photodynamic therapy, PDT, which is a new clinical treatment for cancer that has developed over the past 25 years. In a clinical study of 40 patients with basal cell carcinoma, a malignant type of skin cancer, the Pp IX fluorescence was recorded by a CCD camera set-up. The lesions were treated with ALA cream and thereafter the fluorescence was visualised by using filtered mercury lamps as excitation light-source. The contrast in the fluorescence images was evaluated as a function of ALA application time in order to optimise the technique. The study showed a correlation between the fluorescence images and histological pattern however the individual variations were large. Further studies are planned in order to further improve the technique.

BI-TuP12 Characterization of the Crotalus Durissus Terrificus Venom by Atomic Force Microscopy*, V. Baranauskas, **J. Zhao**,* Faculdade de Engenharia Eletrica e Computacao - UNICAMP, Brazil*; D.M. Dourado,* UNIDEP - Brazil*; M.A. Cruz-Hofling,* Instituto de Ciencias Biologicas - UNICAMP - Brazil, Brazil

Atomic Force Microscopy (AFM) was used to study the morphology of crude venom from the South American rattlesnake Crotalus durissus terrificus. The effects of the crotalic venom on humans are systemic, leading to suffocation in fatal cases due to the neurotoxic, myotoxic and coagulative action of the components of the venom. We used adult snakes from the Pantanal region, Mato Grosso do Sul, Brazil, that remained without food for 30 days before the venom was extracted. The venom was collected manually by a specialist and dried at room temperature. Atomic Force Microscopy images, obtained using low vertical forces, allowed characterization of the surface morphology of the samples at sub-micron resolution. Coiled and porous structures are observed. Characterization of the venom by AFM is potentially of great importance because it may allow the comparison of its natural components. Critical discussion of the experimental results and characterization of the samples by AFM are given.

BI-TuP13 Role of Interfacial Water Structure on the Protein Resistant Properties of Oligo(ethylene glycol) Monolayers*, **B. Subramanian**, J. Yan, G.P. Lopez,* The University of New Mexico

Understanding the mechanism of protein adsorption at surfaces is an important issue in the field of biomedical materials, cellular adhesion and clinical diagnostics. Self-assembled monolayers (SAMs) of oligo(ethylene glycol)-terminated alkanethiols on gold are known to be protein resistant and represent a good model system to study the interactions of proteins with organic surfaces. Although these SAMs are resistant to protein adsorption, the mechanism by which these monolayers prevent protein adsorption is not yet established. Recently, it was suggested that protein resistance of these monolayers is a consequence of the formation of a structured interfacial water layer, which prevents direct contact between the surface and the protein. It was further suggested that, this might be a common mechanism for other monolayers, which show resistant to protein adsorption. It has been observed that, interfacial water undergo sharp changes in its properties (e.g., density, surface viscosity) at 15, 30, 45, and 60°C. These changes are attributed to the change in the structure of interfacial water at that temperature. We examine whether the change in the interfacial water structure at these characteristic temperatures affect the protein resistant properties of these monolayers, by carrying out protein adsorption on mixed monolayers of hexa(ethylene oxide)-terminated alkanethiols and methyl terminated alkanethiol (@chi@ @sub EG6@ = 0.44) as a function of temperature. The results show that, there is a sharp change in the protein adsorption behavior at 30±1°C. Below this temperature, there is no protein adsorption and above this temperature there is approximately a monolayer of protein adsorbed on the SAM surfaces. These results strongly support the view that interfacial water structure plays an important role in the protein resistant properties of oligo(ethylene glycol) SAMs.

BI-TuP16 Oligo(Ethylene Glycol)-Terminated Self Assembled Monolayers: Protein Resistance and the Effect of Assembly Temperature*, C. Boozer, S. Chen, L. Li, S. Jiang,* University of Washington

The rational design of protein resistant surfaces is a critical step in the ongoing development of biomaterials and biosensors, yet we lack a fundamental understanding of how such surfaces work. Here, we report a systematic study of the behavior of oligo(ethylene glycol)-terminated self-assembled monolayers (SAMs) prepared at a range of temperatures. The monolayers were formed by self-assembly of (EG)6-terminated thiols, in a heated (or cooled) methanol solution, on both single crystal and polycrystalline gold films. The films were characterized using atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and infrared adsorption (FTIR). Protein adsorption on the OEG-terminated SAMs was studied using a home-built surface plasmon resonance (SPR) sensor. It was found that the ability of the OEG-terminated SAMs to resist protein adsorption from a buffer solution correlates with the temperature at which they were prepared. Protein adsorption studies were performed with both bovine serum albumin and fibrinogen, and in both cases we found that protein resistance of the films was greatly diminished by increasing assembly temperature. A possible mechanism will be presented.

BI-TuP17 Determination of Adsorption Thermodynamics for Lysine Residues on Functionalized SAMs Using Surface Plasmon Resonance*, V.N. Vernekar, R.A. Latour,* Clemson University

Although protein adsorption is key to many bioengineering problems, it is still not well understood. New comprehensive approaches to this problem are needed. In this study we take a systematic approach to address protein-surface adsorption by studying submolecular interactions of peptide residues with model surfaces. We hypothesize that combining the intermolecular thermodynamic contributions for peptide residue-surface adsorption with intramolecular residue-residue interactions will provide an approach to accurately predict overall protein adsorption. Accordingly, the objective of this study was to develop experimental techniques to measure residue-surface adsorption using surface plasmon resonance spectroscopy (SPR). The model residue-surface system selected for this initial study was poly-L-lysine (PL) and OH & COOH terminated Au-alkanethiol self assembled monolayers (SAMs). Preliminary studies were conducted to develop surface preparation and cleaning protocols necessary to obtain a stable SPR signal during the adsorption process. Adsorption studies were then conducted to measure the difference in signal as a function of surface functionality and PL concentration. Results show that the amount of adsorbed PL increases with increasing solution concentration, with the COOH-SAM adsorbing more PL than the OH-SAM for each concentration. These studies provide experimental data that is needed for calculating thermodynamic parameters for adsorption (Gibbs free energy, enthalpy, entropy) for each of these model systems. These values will be compared to results predicted from computational chemistry studies by others in our group for these same residue/surface systems.

Electronics
Room 134/135 - Session EL-TuP
Electronic Materials Poster Session

EL-TuP1 Fabrication of GaN Blue LED by a Laser Lift-Off(LLO) Method*, D.W. Kim,* Sungkyunkwan University, Korea*; C.H. Jeong,* Sungkyunkwan University, Korea, South Korea*; Y.J. Sung,* Samsung Advanced Institute of Technology*; H.S. Kim,* Samsung Electronics Ltd.*; G.Y. Yeom,* Sungkyunkwan University, Korea

Recently, GaN-based optoeletronic devices such as light emitting diodes(LEDs) and laser diodes(LDs) in blue and ultraviolet wavelength regions have been studied intensively and also fabricated successfully. However, the contacts to GaN-based LEDs are currently made by depositing metal layers on the top of GaN-based LEDs, therefore, significant optical loss is inevitable. In this study, transparent conducting oxide such as indium tin oxide(ITO) was applied to n-GaN after the laser lift off(LLO) of the GaN quantum well device structures. Also, in this device, blanket Pd was deposited as a contact material to p-GaN. ITO and Pd were deposited at room temperature using a conventional electron beam evaporator. Thermal annealing at various temperatures and environments was followed in a tube furnace. The electrical and physical properties of ITO contact to laser lift-off n-GaN and Pd contact to p-GaN were investigated. Contact resistivities and I-V characteristics of the ITO and Pd contacts were measured to estimate the contact and electrical properties of ITO and Pd contacts fabricated on the laser lift-off n-GaN and p-GaN, respectively. The optical properties of the deposited and annealed ITO films were also investigated. GaN LEDs device performance fabricated by LLO was investigated and compared to conventionally prepared GaN-LEDs.

EL-TuP3 Crystal Growth and Characterization of AgAlS@sub 2@ Crystals for Blue Light Emitting Device*, Y. Akaki, H. Komaki,* Miyazaki University, Japan*; M. Yoneta,* Okayama University of Science, Japan*; T. Ikari,* Miyazaki University, Japan

Among ternary chalcopyrite semiconductors, AgAlS@sub 2@ may be promising material for blue light emitting device since the sample is a direct transition type and the bandgap of 3.1 eV at room temperature. However, it is well known that the chalcopyrite semiconductors have many intrinsic defects. The crystal growth of high quality is a difficult because of high melting point and ternary compound. Therefore, reports on the precise material characterizations of the AgAlS@sub 2@ crystals are a few in comparison with other chalcopyrite semiconductors.In this work, the AgAlS@sub 2@ crystals are grown by Hot-Press (HP) method at 400 ~ 700 °C for 1 h under high presser (10 ~ 100 MPa). One of the advantages of the HP method is that a crystal growth is easy at low temperature. The sizes of the samples are 2 cm in diameter. All samples indicate chalcopyrite structures, nearly stoichiometry and n-type by means of X-ray diffraction, electron probe microanalysis and thermoprobe analysis, respectively. In the photoluminescence spectra at liquid nitrogen temperature, donor-acceptor pair emission band may be remarkably observed. The samples have both donor and acceptor-types impurities.

EL-TuP4 Effect of Substrate Position in i-ZnO Thin Film Formation to Cu(In,Ga)Se@sub 2@ Solar Cell*, T. Yamaguchi,* Wakayama National College of Technology, Japan*; T. Tanaka,* Saga University, Japan*; A. Yoshida,* Toyohashi University of Technology, Japan

Heterojunction devices based on Cu(In,Ga)Se@sub 2@ thin films are considered to be one of leading candidates for low-cost photovoltaic power system. Laboratory-size devices by using the three-stage process have exceeded 18% conversion efficiencies.@footnote 1@ We have also attempted to fabricate solar cells based on Cu(In,Ga)Se@sub 2@ thin films by using a thermal crystallization technique for large scale industrial production.@footnote 2@ For improvement in solar cell performance, it is effective to use a buffer layer with the suppression of the leakage current and the decrease in buffer absorption loss. ZnO thin films have attracted considerable attention for buffer films, because of their high resistivity, good optical transmittance from UV to near IR, and low-cost fabrication. In this study, ZnO thin films were prepared by rf magnetron sputtering of non-doped ZnO target in Ar gas under the various substrate positions and their films were applicated to solar cells. We have characterized ZnO thin films and investigated the solar cell performance. The resistivity and the full width at half maximum (FWHM) in XRD diffraction peak were rapidly changed depending on the substrate position. The characteristics of solar cells were correspondent to the change of the resistivity and the FWHM in ZnO thin films. @FootnoteText@ @footnote 1@ M.A.Contreras, B.Egaas, K.Ramanathan, J.Hiltner, A.Swartzlander, F.Hasoon and R.Noufi, Prog. Photovolt. Res. Appl. 7, 300 (1999). @footnote 2@ T.Yamaguchi, T. Kobata, S. Niiyama, T. Nakamura, A. Yoshida, Tech. Digt. of PVSEC-12 (Cheju, 2001) to be published.

EL-TuP5 Optical Characterization of AgInGaS@sub 2@ Crystals for Nonlinear Optical Devices*, K. Itani, H. Komaki,* Miyazaki University, Japan*; S. Chichibu,* Tsukuba University, Japan*; Y. Akaki, T. Ikari,* Miyazaki University, Japan

I-III-VI@sub 2@ chalcopyrite semiconductors have made rapid progress for the solution of environmental and resources problems. CuInSe@sub 2@, especially, CuInGaSe@sub 2@, is expected as solar cell applications since it has large absorption coefficient of about 10@super 5@ cm@super Ð1@ at bandgap energy region. On the other hand, Ag-III-VI@sub 2@ chalcopyrite semiconductors, especially AgGaS@sub 2@, have been investigated as nonlinear optical materials. AgInGaS@sub 2@ is also much attracted as nonlinear optical materials for wide wavelength range.@footnote 1,2@ AgInGaS@sub 2@ has a bandgap energy from 1.9 to 2.7 eV. However, reports on the precise material characterizations of the AgInGaS@sub 2@ crystals are a few in comparison to other Ag based chalcopyrite semiconductors.The AgIn@sub X@Ga@sub 1-X@S@sub 2@ (X=0 ~ 1.0) crystals have been grown by the vertical gradient freezing (VGF) method. All samples indicate chalcopyrite structures, nearly stoichiometry and n-type by means of X-ray diffraction, electron probe microanalysis and thermoprobe analysis, respectively. Lattice constants of a and c axis are proportional with X values, indicating correspond to VegardÕs law. On the other hand, a free exciton (FE) emission band may be remarkably observed in the photoluminescence spectra at 77 K. This means that the samples are high purity. It is clear that the energy of the FE emission band shows a nonlinear dependence on the composition X values. Furthermore, the parameters of the refraction and permittivity also increase nonlinearly with increasing the composition X values. @FootnoteText@ @footnote 1@V. V. Badikov et al., J. Quantum Electron 10 (1980) 1302. @footnotre 2@O. G. Vlokh et al., Sov. Phys. Solid State 27 (1985) 787.

EL-TuP6 P-type Control of Sb-doped CuIn@sub 2@ Crystals for Solar Cell Application*, H. Komaki,* Miyazaki University, Japan*; M. Yoneta,* Okayama University of Science, Japan*; Y. Akaki, T. Ikari,* Miyazaki University, Japan

Among ternary chalcopyrite semiconductors, CuInS@sub 2@ may be the most promising material for photovoltaic applications due to the bandgap of 1.5 eV which perfectly matches the solar spectrum for energy conversion. However, the conversion efficiency of the CuInS@sub 2@ based solar cells are so far limited to around 12 %.@footnote 1@ One reason for this relatively low efficiency is that the physical properties of CuInS@sub 2@ are not accurately known because high-quality single crystal growth of CuInS@sub 2@ is difficult in comparison to CuInSe@sub 2@ and CuGaSe@sub 2@.In this work, the CuInS@sub 2@ crystals are grown by Hot-Press (HP) method at 400 ~ 700 °C for 1 h under high presser (10 ~ 100 MPa). One of the advantages of the HP method is that a crystal growth is easy at low temperature. The sizes of the samples are 2 cm in diameter. All samples indicate chalcopyrite structures, nearly stoichiometry and n-type by means of X-ray diffraction, electron probe microanalysis and thermoprobe analysis, respectively. However, the sample grown at 400 °C has an also different phase (CuIn@sub 11@S@sub 17@). According to increasing temperatures, the sample does not have the different phase. In the photoluminescence spectra at 77 K, donor-acceptor pair emission band may be remarkably observed. The samples have both donor and acceptor-types impurities. Furthermore, p-type CuInS@sub 2@ crystals can be obtained by Sb-dopong. Volume resistivity of the CuInS@sub 2@ crystal increases by increasing the concentration of Sb (less than 0.1 atm. %). The resistivity can be also controlled by concentration of the Sb-doping. @FootnoteText@ @footnote 1@D. Braunger, D. Hariskos, T. Walter and H. W. Schock, Sol. Energy Mater. and Sol. Cells 40, 97 (1996).

EL-TuP7 Focused Ion Beam Induced Damage in the Transmission Electron Microscopy Specimen of Semiconductor Devices*, N. Kato,* IBM Japan, JAPAN*; H. Saka,* Nagoya University, Japan

Focused Ion Beam (FIB) system is indispensable for Cross-sectional Transmission Electron Microscopy (X-TEM) sample preparation, especially when sub-micron spatial accuracy is needed. It is well known that FIB induces damage to the samples. The damage is induced in the etching process as well as in the process of examining the X-section. Earlier study showed that the former does not depend on the etching time or the beam current, and little can be done to reduced the damage other than to use a lower energy FIB. However, the latter varies with the beam conditions, therefore, the examination process can affect the quality of the TEM sample. The purpose of this study is to understand the properties of the damaged layer in order to make a less damaged sample, and exclude the effects of the damage when interpreting TEM images. We studied the damage induced by FIB radiation with smaller current of 1-50 pA at glancing angle of 45 degree, the condition typically used for the examination. We used materials common in semiconductor devices, such as silicon, aluminum, and silicon compounds. We investigated the beam-irradiated surface by X-TEM and Energy Dispersive Spectroscopy (EDS). We found that in the case of crystalline silicon, a few second of beam radiation (< 1 pC/um2) amorphousized the surface. The amorphous layer was 40 nm deep and the gallium concentrates at the outmost 20 nm layer. Radiation of more than a few minutes accumulated a layer consisted of 20 nm carbon rich silicon and 20 nm carbon, silicon and oxide mixture. We found that this layer was made by the re-deposition of the beam-spattered material, which can be reduced by an optimizing the beam condition.

EL-TuP8 A Study on the Germanosilicide Formation in the Ni/Si@sub 1-X@Ge@sub X@ System for CMOS Device Applications*, H.-J. Choi, D.-H. Ko,* Yonsei University, Korea*; J.-H. Ku, C.-J. Choi, S. Choi, K. Fujihara, H.-K. Kang,* Samsung Electronics Co., Korea*; C.-W. Yang,* Sungkyunkwan University, Korea

Si@sub 1-X@Ge@sub X@ has been studied in many applications in order to resolve issues on size reduction in ULSI devices. For the application of Si@sub 1-X@Ge@sub X@ to ULSI devices, interactions with metals such as Co, Ti, or Ni should be investigated to show the SALICIDE process adaptability. In the application of Co, Ti in the Si@sub 1-X@Ge@sub X@ system, it has been reported that the Ge segregation and the film islanding occurs with the addition of Ge, which lead to the increase of gate resistance. Due to its low resistance, leakage current, and no pattern size dependence much attention is focused on the Ni-silicide for sub-100nm technology. Therefore, in this study, the solid-state reaction in Ni/Si@sub 1-X@Ge@sub X@ systems and the thermal stability of Ni/Si@sub 1-X@Ge@sub X@(X=0, 0.16, 0.25, and 0.29) were investigated. The silicidation was performed by RTP from 500°C to 980°C for 30sec under N@sub 2@ flow. Low resistive NiSi phases are not detected above 660°C in the case of Ni/poly-Si systems, while Ni(Si@sub 1-y@Ge@sub y@) phases are observed at above 820°C in Ni/Si@sub 1-X@Ge@sub X@ (X=0.16, 0.25, and 0.29) systems. When Ge is incorporated, germanosilicide on poly-Si@sub 1-X@Ge@sub X@ is unstable due to the formation and growth of Ge rich Si-Ge alloy grains between germanosilicide grains near free surface. This results in a layer inversion of Ni(Si@sub 1-y@Ge@sub y@) and Si@sub 1-X@Ge@sub X@ layers, and consequent increase in Rs values about 10@super 6@@ohm@/sq. above 620°C. Upon higher temperature annealing, the inverted grains grow and finally reach the free surface. Due to the incorporation of Ge, the phase transition to disilicide is delayed in the Ni/Si@sub 1-X@Ge@sub X@ system. Prior to the phase transition, inversion of germanosilicide layers and Si@sub 1-X@Ge@sub X@ layers occurs, which results in sharp increase in sheet resistance values at above 620°C.

EL-TuP9 Positron Annihilation Studies of Defects at Metal-silicon Carbide Interfaces*, P.R. Dunstan,* University of Wales, UK, United Kingdom*; H.M. Fretwell, D. Jones, S.P. Wilks, M. Charlton, D.P. van der Werf,* University of Wales, UK*; A. van Veen, H. Schut,* Interfaculty Reactor Institute (IRI), Netherlands

Positron annihilation has become an important technique for the investigation of vacancy-like defects. The mechanism for the formation of Ohmic and Schottky metal contacts to silicon carbide is not well understood and positron annihilation spectroscopy studies offer a detailed insight into the role of defects at the interface. Our investigations have concentrated on a number of different preparations, each of which produced different I/V characteristics. Chemical cleaning, ultra-high vacuum preparation and in-situ annealing were all addressed and we demonstrated a significant difference in the Doppler broadened S parameter for each type of contact. In particular the presence of fewer defects at Schottky contacts than at Ohmic contacts was apparent. Temperature studies performed were also able to correlate the reduction of defects with the improvement of Schottky I/V characteristics. The results represent a significantly step in understanding and controlling metal contacts to silicon carbide.

EL-TuP10 Effects of Surface Band Bending on Electrical Properties of AlGaN/GaN HFET Observed by I-V and XPS Measurements*, J.-L. Lee,* ***K.J. Choi****, C.M. Jeon,* Pohang University of Science and Technology (POSTECH), Korea*; J.H. Lee,* Kyungpook National University, Korea

Surface states of compound semiconductors are closely related to the undesirable characteristics of FETs such as transconductance dispersion, low breakdown voltage behavior, and low frequency noise. Recently, it was reported that the PL intensity was sharply increased by dipping GaAs wafer under intense light (photowashing treatment), which was explained by the reduction of surface states and the unpinning of surface Fermi-level. No works, however, were conducted on the effects of photowashing treatment on electrical properties of FET, especially AlGaN/GaN HFETs. In this work, we applied photowashing treatment on the ungated surface region between gate and source/drain electrodes of AlGaN/GaN HFETs and observed its effects on electrical characteristics using I-V and XPS. The AlGaN/GaN HFETs with a gate length of 1.0-micron were fabricated. The devices were photowashed by dipping them into deionized water under yellow room light. Photowashing time was varied from 1 to 30 minutes. The surface exposed under the same condition of photowashing treatment was characterized using XPS. In XPS measurement, it was found that the oxide was primarily composed of Al and Ga oxides. In I-V measurements, the drain current at gate biases corresponding to open channel and gate-to-drain reverse leakage current were simultaneously decreased. The decrease of drain current was explained by the increase of depletion width under the ungated surface region between gate and source/drain electrodes. This was evidenced by the decrease of binding energies of Ga 3d and N 1s photoemission spectra, namely, the movement of surface Fermi-level towards the valence band. On the other hand, the decrease of gate-to-drain leakage current was explained by the increase of negatively-charged surface states. From the changes of (Ga+Al) to N ratio at the surface of AlGaN by the treatment, the most probable point defect responsible for the movement of surface Fermi-level was discussed.

EL-TuP11 Structural and Electrical Characteristics of CVD-CoSi2/Si0.83Ge0.17/Si(001)*, **S.H. Ban**, Y.S. Ahn, D.O. Shin, N.-E. Lee,* Sungkyunkwan University, Korea*; B.T. Ahn,* Korea Advanced Institute of Science and Technology*; K.-H. Shim,* Electronics and Telecommunications Research Institute, Korea

Silicide formation on SiGe alloys has been studied for low-resistance contacts and Schottky barrier contacts for various applications. Among the various silicides, CoSi@sub2@ is a very attractive material due to its low resistivity, one of the more promising candidates for making high performance Schottky barrier devices, and possibility of self-aligned silicide formation at relatively low temperatures. Recently, there have been several investigations on CoSi@sub2@ deposited by molecular beam epitaxy on SiGe alloys or silicidation of sputter-deposited Co layers on SiGe alloys, but no reports on CoSi@sub2@ deposited by CVD on SiGe alloys so far as we know. In this study, we investigated structural and electrical properties of CVD-CoSi@sub2@/Si@sub0.83@Ge@sub0.17@/Si(001) contacts by structural, chemical, and electrical analyses. Uniform cobalt disilicide (CoSi@sub2@) layers has been grown in-situ at 100 mTorr on p-type and n-type Si@sub0.83@Ge@sub0.17@ grown on p-type Si(001) by metal organic chemical vapor deposition (MOCVD) at 600 °C using cyclopentadienyl cobalt, Co(h@sub5@-C@sub5@H@sub5@)(CO)@sub2@ with 10 sccm of H@sub2@ carrier gas. The interfacial, structural, and chemical properties of MOCVD-CoSi@sub2@/Si@sub0.83@Ge@sub0.17@ were analyzed by x-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), Rutherford backscattering spectroscopy (RBS), and Auger electron spectroscopy (AES). The effective Schottky barrier heights and electrical properties of CVD-CoSi@sub2@/Si@sub0.83@Ge@sub0.17@/Si(001) were measured by current-voltage (I-V) measurement and the sheet resistance measurement, respectively. The measured effective Schottky barrier heights are in the range of 0.55-0.60 eV for CVD-CoSi@sub2@/n-Si@sub0.83@Ge@sub0.17@/Si(001) without showing significant dependence of measured fBn on the annealing temperature, Ta = 450 °C to 800 °C.

EL-TuP12 On the Induced Net Charge Density at ICB Deposited MS Interface*, **B. Cvikl**,* J. Stefan Institute, Slovenia

The origin of the so called excess capacitance of non ideal Schottky junctions has remained unclear for well over the past decade. Recently we have shown,@footnote 1@ utilizing the series of Ag/Si and Pb/Si Schottky junctions deposited by the ionized cluster beam, ICB, method as obtained for different values of external metal ions acceleration voltages, that the origin of the reverse biased excess capacitance is directly related to the occurrence of induced net charge density. This induced net charge density occurs at the, with the penetrating metal ions, enriched Si substrate-Si interface, and its magnitude appears to be a deposition method sensitive. It is the external bias dependence of this induced interfacial net charge, to a very good approximation described by a gaussian curve, which appears to be responsible for the bias dependent excess capacitance in the reverse direction if the junction series resistance is small and in the forward direction if it is not. From the above data extracted analytical expression for the effective density of interface electronic gap states is characterized by numerous sharp spikes the envelope of which exhibits strong, standing wave like oscillations accompanied with nodes. This behavior is strikingly similar to the shape of local density of states of a one dimensional lattice of N identical interacting atoms placed in an external uniform electric field, exhibiting the well known Wannier-Stark ladders.@footnote 2@ In this presentation the possible manifestation of the Wannier-Stark effect in ICB deposited Schottky junctions will be analyzed and the possibility for potential application of the observed effect for certain simple devices will be discussed. @footnote 1@ B. Cvikl and D. Korosak, Vacuum 61 (2001) 355. @footnote 2@ S. G. Davison et al., J. Phys.: Condens. Matter 9 (1997) 6371.

EL-TuP13 Electrical Properties of Cd Vapor Pressured CdZnTe for HgCdTe Passivation*, **S.Y. An**,* Korea Institute of Science and Technology, seoul korea

The semiconductor-passivating layer interfaces, as well as the dielectric properties of the passivating layers, play important roles in HgCdTe based photodiodes. Various techniques are being developed to obtain surface passivation layers on HgCdTe, but the thermal or e-beam evaporation methods have become the general approach in this area. When CdZnTe films deposited with an evaporation techniques, it might have a possibility to introduce surface nonstoichometry due to high vapor pressure of group II element. To avoid surface nonstoicheometry in deposited CdZnTe layer, we intentionally exposed Cd overpressure from 1x10@super -4@ torr to 1x10@super -8@ torr when the CdZnTe deposition was carried out. Test structures of Metal-Insulator-Semiconductor were processed and their electrical properties were measured by capacitance-voltage characteristics. For the Cd pressure of 1x10@super -8@ torr, the flat band voltage of MIS capacitor is about -0.3V with fixed charge density of 3.0x10@super 10@/cm@super -3@ and hysteresis was drastically reduced. We found that Cd vapor pressured CdZnTe passivation layer have much lower fixed charge density, small hysteresis and nearly zero flat band voltage.

EL-TuP14 A Study of Iron-Contaminated p-type Silicon by Scanning Probe Microscopy*, **M.N. Chang**,* National Nano Device Laboratories, Taiwan, R. O. C.*; T.Y. Chang,* National Chiao Tung University, Taiwan, R. O. C.*; C.Y. Chen, F.M. Pan, B.W. Wu,* National Nano Device Laboratories, Taiwan, R. O. C.*; T.F. Lei,* National Chiao Tung University, Taiwan, R. O. C.

One significant factor that degrades a Si device's performance and its yield is metallic contamination. Among the metallic contaminants, Fe has been the most extensively studied, because it is commonly observed as a dissolved impurity in Si wafers and, in comparison with other metallic contaminants, is more difficult to getter. In addition, it is also hard to observe the micro-distribution of oxidation related defects induced by slightly Fe contamination. In this work, we have employed scanning probe microscopy to investigate the distribution of oxidation related defects in the Fe-contaminated p-type Si wafers, on which a thermal oxide layer of 40 Å was grown. All of the p-type Si wafers was contaminated by a nitrate solution of a low Fe contaminant concentration, simulating the influence of Fe contamination during the cleaning process. From scanning capacitance microscopy (SCM) studies on the 10-ppm Fe-contaminated samples, a defect region exhibits a lower dC/dV signal than the surrounding normal area at a low bias voltage. According to contact-mode atomic force microscopy (AFM), the surface morphology has little effect on the SCM signal. This is attributed to the positive trapped charges (PTC), which are closely related to negative shift in the flat band voltage and affect the dC/dV value. In the defect region, two small areas about 0.1 µm in size have the lowest SCM signal, suggesting that these two areas have the highest PTC density. One can expect that these two areas would be the most likely weak points, where significant current leakage and oxide breakdown can occur at a high gate bias. When the contaminant concentration is increased, SCM observed more PTC regions.These results imply that SCM is capable of detecting the position of weak spots in silicon wafers, which may lead to leakage and breakdown problems in gate oxide.

EL-TuP15 Effect of Surface Clean on CVD SiGe Growth*, **J.-S. Maa**, D. Tweet, S.T. Hsu,* Sharp Laboratories of America

Low temperature growth of CVD SiGe was found very sensitive to surface condition. Proper preparation of surface in HF dip or DI rinse is essential to control the SiGe film quality. SiGe films were characterized by high-resolution x-ray diffraction, the effect of surface clean was revealed by the sharpness of the periodic modulation of peaks. SiGe formed on poorly prepared surface resulted in a diffraction pattern with mostly washed out peaks indicating poor crystallinity or a rough surface. The quality of SiGe film was correlated to trace contamination at interface as demonstrated by SIMS. Procedures of surface preparation, including wet process and in-situ vapor etch, and their effects on film quality will be discussed.

EL-TuP16 The Behavior of Dopant Boron during TiSi@sub2@ Formation*, **Y.S. Chung**,* Samsung Advanced Institute of Technology, Korea*; H.S. Park,* Samsung Electronics Co., LTD, Korea*; J.Y. Won, J.M. Choi,* Samsung Advanced Institute of Technology, Korea

The TiSi@sub 2@ formation by plasma-enhanced chemical vapor deposition (PECVD) and the reaction of B doped Si with the overlaying silicide were investigated by X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and secondary ion mass spectroscopy (SIMS). TiSi@sub 2@ with C49 phase was formed on Si substrate at 630°C using TiCl@sub 4@ source gas. The reaction of dopant boron implanted in Si with the silicide leads to the formation of TiB@sub 2@ at the TiSi@sub 2@-Si interface, which was confirmed by XPS and SIMS. The bonding of Ti-B at the interface resulted in the increase of the contact resistance. The effects of heat treatment in TiSi@sub2@ growth and boron behavior also will be discussed.

EL-TuP17 The Investigation of Electroless-plated Copper on TaN/Si as Self-catalyzed by MEVVA Ion Implanter*, **U.-S. Chen**,* National Tsing Hua University, Taiwan*; J.-H. Lin,* National Tsing Hua University, Taiwan, Taiwan, ROC*; W.-J. Hsieh, P.-S. Shih, H.C. Shih,* National Tsing Hua University, Taiwan

This work attempts to implant Cu ions into TaN/Si as catalyst by using metal vapour vacuum arc (MEVVA) ion implanter for electroless Cu plating.

The range of dose is between 5.0¡Ñ10@super 15@ and 1.0¡Ñ10@super 17@ ions/cm@super 2@. Ion energy is from 40 to 50 keV. These specimens were subsequently deposited with a thin layer of Cu in an electroless bath developed by this group. Furthermore, the electroless plated copper films were studied by SIMS, SEM, four point probe for electric resistivity, XRD and a mechanical pull-up test. First of all, a noticed relationship between SIMS depth profiles and ion energy is established. All the sheet resistance of specimens are lower than 1.85 µm@ohm@-cm after 300°C annealing for 1 hour. An excellent step coverage and gap filling in sub-micron trench/via were observed by FESEM. The result also indicated that the higher the ion dose/energy, the larger value of adhesion as we obtained from the pull-up test.

EL-TuP18 Selective Electroless-Plated Copper for Deep Sub-micron Interconnect Metallization Through the Catalytic Effect of Cu/ Pd by PIII*, **J.-H. Lin,*** National Tsing Hua University, Taiwan, Taiwan, ROC*; W.-J. Hsieh, X.-W. Liu, C.-S. Kou, H.C. Shih,* National Tsing Hua University, Taiwan

The major goal of this study is to combine the techniques of using plasma immersion ion implantation (PIII) to implant Pd or Cu as a catalyst seed layer onto a TaN diffusion barrier layer and electroless plated Cu to accomplish the ULSI interconnection metallization. Both patterned and blanked wafers were employed using Pd or Cu as catalyst by PIII after which copper was electroless plated on a TaN/FSG/Si multi-layer structure. Either Pd or Cu atoms were sputtered from a negatively biased target and ionized in an argon inductively coupled plasma (ICP). The metal ions were adequately implanted into the substrate with a highly pulsed negative bias (~4000 V). The observation of FESEM indicated that under the circumstances of higher substrate bias voltage and plasma ionization, the electroless copper grows upward from the bottom of the vias (width: 0.25 µm; aspect ratio: 7) layer by layer, with an excellent gap filling ability without the final centered seam. The result of the pull-up test, showed that higher substrate bias and higher plasma density to implant Cu as seed layer can effectively enhance the adhesion strength between electroless-plated copper film and TaN layer.

EL-TuP19 The Morphology and Strain-induced Defect-structure of Ultrathin Epitaxial Fe Films Grown on Mo(110)*, S. Murphy, D. Mac Mathuna, G. Mariotto, **I. Shvets,*** Trinity College, Ireland

The magnetic properties of ultrathin epitaxial Fe and Ni films can often be strongly subject to the film strain imposed by lattice mismatch with the substrate and the mechanisms by which this strain may be relieved. In this work, the morphology and defect-structure of Fe films grown with mismatch m = -8.9% on the Mo(110) surface was characterized by a combination of scanning tunneling microscopy, low-energy electron diffraction and Auger electron spectroscopy. Fe films in a thickness range of 0.5 @<=@ d @<=@ 8 Å were grown on a Mo(110) at substrate temperatures lying in the 300 @<=@ T @<=@ 525 K interval. Near room-temperature, films grow layer-by-layer through a combination of step-flow and two-dimensional island growth until the first two Fe layers are complete. Beyond this coverage, there is a transition to layer-plus-island growth. The first layer is pseudomorphically strained, but the film strain is partially relieved in the second layer by the formation of dislocation lines along the [00-1] direction. Because the film is relaxed in the local region about these dislocations, they form preferential sites for nucleation of third layer islands. The build-up in strain with increasing film thickness results in the formation of a strain-relieving dislocation network in the third layer of the film. At elevated temperatures (495 @<=@ T @<=@ 525 K), the first two Fe layers grow by the step-flow mechanism, leading to the formation of arrays of Fe nanostripes. Dislocations are formed along the [00-1] direction in second layer stripes that are wider than approx. 100 Å. At higher coverages, the Fe agglomerates into large wedge-shaped islands surrounded by an Fe monolayer sea. A dislocation network is formed on these islands, originating in the second layer and persisting to the maximum island thickness observed (approx. 10 layers). This network has a similar structure to that observed on islands grown near 300 K, but is 14% more relaxed along the [1-10] direction.

EL-TuP22 Codoping of Magnetron-Sputter Deposited ZnS:TbOF with Ce for Electroluminescent Phosphors*, J.P. Kim, **M.R. Davidson,*** University of Florida*; D. Moorehead,* Uniroyal Optoelectronics*; M. Puga-Lambers,* University of Florida*; Q. Zhai,* CORNING Lasertron*; P.H. Holloway,* University of Florida

RF magnetron-sputter deposited ZnS:TbOF thin film electroluminescent (EL) phosphors 1mm ± 10% thick were codoped with Ce and the EL performance tested with 60Hz trapezoidal voltage pulses. The B40 of Ce codoped ZnS:TbOF films annealed at 500°C for 60 minutes was 144 cd/m@super 2@ compared to 86 cd/m@super 2@ for undoped ZnS:TbOF films. Further analysis using XRD, SEM and AFM showed no changes in crystallinity or surface morphology and SIMS analysis showed the Ce concentration to be far below Tb concentration. Electrical Q-V, C-V and L-V measurements indicate that there are changes in the electron transport suggesting that the increase due to Ce codoping of ZnS:TbOF film is likely due to modified space charge in the ZnS:TbOF ilm.

EL-TuP23 Improved Efficiency and Space Charge Effects in ZnS:Mn ACTFEL Devices Co-Doped with KCl*, **J.S. Lewis,*** MCNC*; M.R. Davidson, Q. Zhai, K. Waldrip, P.H. Holloway,* University of Florida

Alternating-current thin-film electroluminescent (ACTFEL) phosphors have been studied and improved with respect to brightness, efficiency, and stability. It is shown that ex-situ co-doping of the sputter deposited ZnS:Mn active layer with K and Cl results in 53% improvement in brightness, 62 % improvement in efficiency, and better 100-hour accelerated aging stability. This improvement was demonstrated to result from a 75% increase in excitation efficiency for conduction electrons, combined with a small decrease in both light outcoupling and non-radiative recombination. By studying the electrical behavior of the co-doped devices as compared to the undoped devices, it was determined that there is a reduced amount of static space charge in the films, resulting in a larger average field, increased excitation efficiency, and increased charge multiplication. The reduced space charge is attributed to the addition of charge compensating zinc vacancy-chlorine complexes and isolated chlorine point defects, which are acceptor and donor defects, respectively, and the reduction of zinc vacancy deep hole traps. It is postulated that there is sufficient electron multiplication or donor ionization to create a situation in which the current limit is set by the phosphor resistance rather than a capacitance or density of states. The increased efficiency is discussed in a framework of generic ACTFEL device efficiency common to all ACTFEL phosphors. Work supported by DARPA Grant # MDA97-1-0003 through the Phosphor Technology Center of Excellence.

EL-TuP24 Dry Etching of Sapphire for the Device Isolation using BCl@sub3@/Cl@sub2@(SiCl@sub4@) Inductively Coupled Plasmas*, **C.H. Jeong,*** Sungkyunkwan University, Korea, South Korea*; D.W. Kim, J.H. Kim,* Sungkyunkwan University, Korea*; Y.J. Sung, S.H. Chae, J.S. Kwak, Y.J. Park,* Samsung Advanced Institute of Technology, Korea*; G.Y. Yeom,* Sungkyunkwan University, Korea

Sapphire wafer has been used in the optoelectronics industries as the substrates due to its high chemical and thermal stability. One of the problems in using sapphire wafers to optoelectronic devices such as GaN-based devices is the difficulty in cutting and backside mechanical polishing after completing the device due to the differences in the crystal orientation and the hardness of sapphire itself. Especially, to obtain reliable device isolation, more than 50 wide scribe line width is required for mechanical cutting using a diamond wheel or for scribing using a diamond scriber. However, if the device isolation can be replaced by dry etching followed by the separation of the devices by rolling and stretching, the scribe line width could be reduced to 5 and the yield per wafer could be also increased by 30%. In this study, BCl@sub3@/ SiCl@sub4@ and BCl@sub3@/Cl@sub2@ based inductively coupled plasmas have been used to etch (0001) sapphire wafers to obtain the etch rates over 400nm/min and the influence of the additive gases such as Ar, Kr, HBr, etc. on the sapphire etch characteristics were studied. The etch mechanism of sapphire was also investigated by plasma diagnostics and surface analysis using optical emission spectroscopy during the sapphire etching and X-ray photoelectron spectroscopy after the etching, respectively. For the device isolation, the etch profile containing severe notching is greatly encouraged contrary to the etch profile required for semiconductor devices. The degree of notching on the etch profile was observed as a function of process parameters by scanning electron microscopy and the surface roughness was examined by atomic force microscopy before and after the etching of the samples.

EL-TuP25 Etching of CeO@sub 2@ Thin Films in CF@sub 4@/Cl@sub 2@/Ar Plasma*, C.I. Kim, C.S. Oh, D.P. Kim,* Chung-Ang University, Korea*; **C.I. Lee,*** An-San College of Technology, Korea*; T.H. Kim,* Yeojoo Institute of Technology, Korea*; E.H. Kim,* Cheju National University, Korea*; E.G. Chang,* Chung-Ang University, Korea

Cerium dioxide was used as the intermediate layer between the ferroelectric thin film and Si substrate in a metal-ferroelectric-semiconductor field effect transistor (MFSFET), to improve the interface property by preventing the interdiffusion of the ferroelectric material and the Si substrate. In this study, CeO@sub 2@ thin films were etched with a

CF@sub 4@/Cl@sub 2@/Ar gas combination in inductively coupled plasma (ICP). The CF@sub 4@/(CF@sub 4@+Ar) was fixed at 0.2, and the CeO@sub 2@ thin films were etched by adding Cl@sub 2@. Etching properties of CeO@sub 2@ were measured according to the various etching parameters such as radio frequency power (400~600 W), direct current bias voltage (-150~-300 V), and chamber pressure (10~20 mTorr). Chemical reaction of etched CeO@sub 2@ thin films was investigated with x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). In order to analyze the effect of radical density of F, Cl and ion current density as a function of Cl@sub 2@ percentage in CF@sub 4@/Ar, optical emission spectroscopy (OES) and single Langmuir probe were used. The profile of etched CeO@sub 2@ thin films investigated with scanning electron microscopy (SEM).

EL-TuP26 Near-zero-thickness Molecular-layer Diffusion-barriers for Interconnect Applications*, **G. Ramanath**, K. Chanda,* Rensselaer Polytechnic Institute*; X. Guo,* Rensselaer Polytechnic Institute, us*; M. Stukowski,* Rensselaer Polytechnic Institute*; S. Nitta,* IBM Microelectronics

Ultrathin diffusion barriers that can conformally coat sub-100-nm-diameter vias--to allow a greater via fraction for low resistivity Cu--are necessary to fully realize the full potential of Cu technology. Here, we demonstrate the use of <2-nm-thick self-assembled molecular layers (SAMs) as effective barriers to Cu diffusion into SiO@sub 2@. Cu/SiO@sub 2@/Si(001) metal-oxide-semiconductor (MOS) capacitors, with and without SAMs at the Cu/SiO@sub 2@ interface, were investigated during bias-thermal annealing at temperatures between 100-300 °C in a 2 MV/cm electrical field. Capacitance-voltage and current-voltage measurements of MOS capacitors with SAMs having aromatic terminal groups consistently show as much as 5 orders of magnitude lower leakage currents and a factor of 4 higher mean-time-to-failure when compared with the corresponding values measured from uncoated samples. SAMs with short tail lengths or aliphatic terminal groups are ineffective in hindering copper diffusion, suggesting that molecular length and chemical configuration are key factors in determining the efficacy of SAMs as barriers. In addition to the temperature dependence of the barrier properties of SAMs, we will also present preliminary results pertaining to their deposition and behavior on SiLK. Our results will be discussed in the context of microelectronics device processing and integration, to evaluate the utility of ultrathin molecular layers in future interconnect structures.

EL-TuP27 Effect of Interfacial Underlayers on Electromigration in Epitaxial Cu(001) Lines*, **R. Goswami**, H.S. Goindi, H. Kim, M.J. Frederick, G. Ramanath,* Rensselaer Polytechnic Institute*; C.-S. Shin, I. Petrov, J.E. Greene,* University of Illinois, Urbana

The effects of grain size, preferred orientation, and interfacial layers on electromigration (EM) in Cu lines are not yet well understood. In order to isolate the effect of the underlayer and grain structure, we investigate the EM behavior of epitaxial Cu(001) lines on Ta, TaN, and TiN underlayers. Accelerated EM tests were carried out on 2-µm-wide lines with a 3.5 MA/cm@super 2@ current density at temperatures between 200-300 °C. Cu(001) lines on TiN or TaN shows up to a factor-of-10 higher mean-time-to-failure when compared with those on Ta. The superior EM resistance of lines on nitride underlayers correlates with a higher crystal quality--measured by X-ray diffraction--of the Cu epilayers. This correlation is also observed in preliminary experiments of Cu films with slightly different epilayer-quality, deposited on the same underlayer. The activation energy of EM-induced failure of Cu lines on the nitrides is ~0.9 eV, which is significantly higher than the value of ~0.2 eV, observed for Cu(001) on Ta. Our results suggest that orientation inheritance is an important factor that determines the EM lifetime. Based upon these results, we discuss the EM failure mechanism in the context of epitaxial film microstructure, Cu-underlayer interface, and failure morphology revealed by scanning and transmission electron microscopy (SEM and TEM)measurements.

EL-TuP29 Vaporization Characteristics for Liquid Precursor of Cu-CVD*, **S. Akiyama**, A. Sekiguchi, K. Yamada, K. Sekiya, T. Sasaki,* ANELVA Corporation, Japan

A liquid precursor vaporizer used in Cu-CVD equipment for semiconductor metallization was studied. Important issues are high rate vaporization at low temperature around 70°C, suppression of decomposition of the precursor, quick response, and stability. One of equipments made on an experimental basis consists of a rectangular aluminum with about a 22 cm * 7 cm warm section inclined by a certain angle from the horizontal line, where liquid precursor was supplied to spread on the surface and Ar was separately supplied as carrier gas. With inclination angle of 5°, sufficiently high vaporization rate of 2.4 g/min for Cu(hfac)(tmvs) could be obtained at 70°C, 500 Pa. Investigated parameters effective on vaporizing ability were inclination angle, total pressure, and temperature of warm section. Vaporization rate for Cu(hfac)(tmvs) was measured at inclination angle between horizontal line and 30°, at pressure between 330 and 500 Pa, and at temperature between 55 and 70°C. The vaporization rate at 5°, 500 Pa, and 70°C was 43.3 mg/(min)(cm@super 2@). It increased to 60.7 mg/(min)(cm@super 2@) by increasing the angle to 15°, and increased to 88.9 mg/(min)(cm@super 2@) by decreasing the pressure to 330 Pa. Even at lower temperature of 60°C, 21.7 mg/(min)(cm@super 2@) was obtained. In order to obtain the required precursor flow rate, the vaporization surface area have to be obtained, which is based on the vaporization rate for each method. In this case, a vaporization surface area of 57.7 cm@super 2@ was required to achive a deposition rate of 100 nm/min for 300 mm wafer.

EL-TuP31 Preferred Growth of Cu Thin Films on Ta and TaN@sub x@ Diffusion Barriers*, **J.H. Wang**, J.C. Hu, L.J. Chen,* National Tsing Hua University, Taiwan, R.O.C.*; Z.C. Lu, C.S. Hsiung, W.Y. Hsieh, T.R. Yew,* United Microelectronics Corporation, Taiwan, R.O.C.

Ta and TaN@sub x@ films have recently been extensively investigated to substitute for TiN films as an adhesion and diffusion barrier in Cu metallization for ultralarge-scale integrated applications. The electromigration resistance is sensitive to the texture of Cu films. Seeding and controlled growth of Cu films on the underlaying Ta and TaN@sub x@ films might be beneficial in achieving the desired texture of Cu films. In the present work, a series of textured growth of Cu films on the Ta and TaN@sub x@ with varying x was investigated. The phases formed in Ta and TaN@sub x@ films deposited with pure Ar, 10%, 20%, 30%, 40%, 50%, and 60% N@sub 2@/Ar ratios were found to be a mixture of @beta@-Ta and bcc-Ta, bcc-Ta, bcc-TaN@sub 0.1@, expanded bcc-TaN@sub 0.1@, hcp-Ta@sub 2@N, fcc-TaN, and fcc-TaN (nearly amorphous), respectively. The results indicated that the N atoms in Ta and TaN@sub x@ films occupied the interstitial sites of the crystal lattice. Solubility of N atoms in bcc-Ta films is low. The lattice in the vicinity of each atom is severally strained to accommodate the interstitial N atoms. As a result, the structures of bcc-TaN@sub 0.1@ and expanded bcc-TaN@sub 0.1@ are highly distorted. Moreover, the crystal structure of TaN@sub x@ films was found to change from bcc to fcc with increasing N content. A larger interstitial spacing in fcc lattice is capable of accommodating more N atoms in the Ta and TaN@sub x@ lattice. On the other hand, the growth of Cu was found to depend strongly on the microstructures of the Ta and TaN@sub x@ underlayers. The Cu (111)/(200) intensity ratio decreased with the concentration of N in Ta and TaN@sub x@ films. The results are explained in terms of the strained structures of bcc-TaN@sub 0.1@ and poor crystallinity of hcp-Ta@sub 2@N and fcc-TaN.

EL-TuP32 Formation of Titanium Silicides on Silicon-on-Insulator Wafers*, **C.H. Liu**, C.J. Tsai, L.J. Chen,* National Tsing Hua University, Taiwan, R.O.C.

With continuing reduction of device feature size and increase of electronic component density in integrated circuit (IC) technology, SOI (silicon-on-insulator) is going to be the future substrate frame. The conventional advantages arising from SOI device structure and physics are high-speed operation due to low junction capacitance, no latch-up due to dielectric isolation, improved soft-error due to small junction area, reduced power consumption, harsh environment tolerance, and simplified fabrication process. As the CMOS device feature size scales down, formation of low resistivity silicides becomes increasingly difficult. Motivated by the effects of stress state of the metal-silicon diffusion couple on the silicide formation, especially on the silicon surface in SOI material, the influence of stress on silicide formation has been investigated. The SOI wafers used are separation by implantation of oxygen (SIMOX) wafers with a 1900-Å-thick buried oxide (BOX) layer located between the top silicon layer (with variant thickness range 1000~3000 Å) and bottom substrate. The in-situ stresses during reactions, with 5 °C/min ramping rate at 2~5 x 10@super -6@torr, were measured by a scanning laser beam reflection technique. Tensile stress was induced in the top silicon layer. The stress was found to increase with thinner silicon layer. The change is attributed to the difference in the thermal expansion coefficient between SiO@sub 2@ and Si. For the interfacial reactions of Ti on top silicon layer, the C49 to C54 TiSi@sub 2@ phase transformation on SOI wafers was found to be enhanced. The results are discussed in term of the variation of diffusivity of reacting species with the multi-layer stress state.

EL-TuP33 Diffusion Barrier Properties of Metallorganic Chemical Vapor Deposited Niobium Nitride Films Against Cu Metallization*, **C.W. Wu,*** National Tsing Hua University, Taiwan, ROC, Taiwan, R.O.C.*; W.C. Gau,* National Tsing Hua University, Taiwan, ROC*; J.C. Hu,* National Tsing Hua University, Taiwan, ROC, Taiwan, R.O.C.*; T.C. Chang,* National Sun Yat-Sen University, Taiwan, ROC, Taiwan, R.O.C.*; C.H. Chen,* Namat Technology Co., LTD., Taiwan, ROC*; C.J. Chu,* Namat Technology Co., LTD., Taiwan, ROC, Taiwan, R.O.C.*; L.J. Chen,* National Tsing Hua University, Taiwan, ROC, Taiwan, R.O.C.

Amorphous NbN@sub x@ films were deposited by metallorganic chemical vapor deposited (MOCVD) using ethylimidotris(diethylamido)niobium(V) [Nb=NEt(NEt@sub 2@)@sub 3@] source with and without NH@sub 3@ at various temperatures. The diffusion barrier properties of NbN@sub x@ films for Cu metallization were investigated. In the MOCVD system, the precursor was introduced to reaction chamber by a bubbler with Ar as a carrier gas. Both deposition temperature and resistivity of the film was found to decrease drastically upon the addition of NH@sub 3@. The activation energy for the surface reaction was measured to be 0.82 eV in the temperature range of 500- 600°C and decreased to 0.23 eV by adding 20 sccm NH@sub 3@ in the temperature range of 300 - 400°C. The NbN@sub x@ films was found to be amorphous by X-ray diffractometry (XRD) and transmission electron microscopy (TEM). Concentration-depth analysis was carried out by Auger electron spectroscopy (AES). The concentration of C in films was reduced significantly and the concentration ratio of N to Nb was varied from 1.67 to 1.10 by using NH@sub 3@ as a reactant gas. From XRD and SEM observation, it was found that 50-nm-thick NbN@sub x@ film can effectively prevent penetrating of Cu in samples annealed at 550°C for 30 min. In samples deposited with 20 sccm NH@sub 3@, the barrier survived in samples annealed at 600°C for 30 min. The higher thermal stability of the films deposited with NH@sub 3@ is correlated to presence of N atoms in the NbN@sub x@ barrier films.

EL-TuP34 On Thermostability of Sulphur Complexes with Metals of Transition Group in Silicon*, M. Arzikulova, **E.U. Arzikulov,** T.U. Tashbaev, S.N. Sradjev,* Samarkand State University, Uzbekistan

Under determined conditions of doping p-Si (@rho@ = 10 @Ohm@ cm) Sulphur and both Cd and Zn all electric active atoms form electric neutral complexes among ach other. Electrical properties of the material are reimbursed in this case. Influence of heat treatment (HT) at different temperatures on stability of the complexes and determination of their effect on thermic flaw generation are investigated in the paper. Si samples were doped consequently with S, Cd, Zn at effective temperatures of complex formation among the impurities. The samples were treated at 100 - 1150 ° for 1 h after doping. Resistiveties of the samples were measured after each cycle of the treatment. Si(B,S), Si(B,Cd), Si(B,Zn) samples were also treated under the same conditions for comparison purposes. Results showed that before HT parameters of Si(B,S,Cd), Si(B,S,Zn) samples are comparable with those of before doping: p-type of conductivity and @rho@ = 10 @Ohm@ cm. We consider that all electrically active S, Cd, Zn atoms are bounded in electrically neutral complexes. Their concentration according to calculations are N@sub Cd@ = 2x10@super 16@ cm@super -3@ N@sub Zn@ = 2x10@super 16@ cm@super -3@ and the rest of S atoms are in nonequilibrium states in the dissociation centers. We conclude that first of all electric neutral S, Cd, Zn atoms are stable enough up until 1100 °. At the temperatures above partial or total dissociation takes place and properties of the material are determined by Si atoms. Secondly, formation of the electrically neutral complexes prevents thermic flaws generation.

EL-TuP35 The Theory of Multiphonon Resonant Raman Scattering in a Quantum Well*, **A. Eshpulatov,*** Samarkand State University, Uzbekistan

The theory of multiphonon resonant Raman scattering (MPRRS) with the partisipation of the quasi-two-dimensional (Q2D) excitons as intermediate states is developed ffor a quantum well (QW). It is shown that the scattering cross section is proportional to (. (is the dimensionless exciton-LO-phonon coupling constant) in the maximum of the scattering peak. It means that the obtained contribution into cross section is essentially bigger than the contribution of free electron-hole pairs (EHP) in the Q2D system@footnote 1@ and than the contribution of 3D-excitons in bulk semiconductor.@footnote 2@ The enhancement of the MPRRS in comparision with the bulk case is explaned by the possibility of the real LO-phonon emission in QW in the frequency region (corresponding to the direct creation or direct annihilation) while in the bulk semiconductor two phonon scattering consists from two indirect processes- creation and annihilation of exciton. The enhancement of the scattering in comparision with the EHP as the intermediate states sown that into the Q2DS the excitonic mechanism of MPRRS dominants. It is justified especialy in the case of two-phonon resonant Raman scattering when the exciton presents only in the act of the indirect creation (or indirectannihilation) and monoemission of the LO-phonon. @FootnoteText@@footnote 1@L.I. Korovin, S.T. Pavlov & B.E. Eshpulatov, Pis'ma Zh. Eksp. Teor. Fiz. 51, 516, (1990); [JEPT Lett., 51, 584, (1990)]. @footnote 2@A.V. Goltsev, I.G. Lang, S.T. Pavlov M.F. Bryzhina, J. Phys. C., 63, 4221 (1983).

EL-TuP36 Scanning Spreading Resistance Microscopy Bias Dependence of Doped III-V Semiconductors*, **R.P. Lu,*** University of California, San Diego*; K.L. Kavanagh,* Simon Fraser University, Canada*; St.J. Dixon-Warren, A.J. SpringThorpe, R. Streater,* Nortel Networks, Canada

Scanning Spreading Resistance Microscopy profiling of III-V optoelectronic devices has been previously demonstrated. It is clear that the physical interactions between the SSRM tip and the semiconductor sample are not well understood. The overall measured SSRM resistance is the sum of the spreading resistance and contact resistances. To obtain a better understanding of the role of the contact resistance, we have conducted SSRM measurements of current as a function of sample bias for a large dynamic range of doping densities (10@super 16@ - 10@super 19@ cm@super -3@). For this paper, we propose a model based on Fermi level pinning. Theoretical calculations correlate well with experimental SSRM results for both GaAs and InP.

EL-TuP37 Recombination Properties of Heavily Doped GaAs*, **R.K. Ahrenkiel,** W. Metgzer, R. Ellingson,* National Renewable Energy Laboratory*; D.I. Lubyshev, W.K. Liu,* Quantum Epitaxial Designs, Inc.

Heterojunction bipolar transistors (HBTs), using GaAs as the base, have become a technology of great importance for high speed communications. The base of the high-speed GaAs transistor is carbon doped to levels between 1x10@super 19@ and 1x10@super 20@ cm@super -3@ and the electron lifetime in the base is critical to amplifier gain. The classical band-to-band Auger effect varies as the inverse square of the free-carrier concentration. We have, for the first time, directly measured this lifetime over a wide doping range, using the up-conversion method of time-resolved photoluminescence. With this method, we were able to measure carrier lifetimes as short as 100 fs. The free hole concentrations, (p), were measured by the Hall effect and the carbon concentrations by the SIMS method. The data showed that acceptor activation was nearly 100 percent, even at 78 K. Photoconductive decay and photoluminescence data show bandgap shrinkage that is attributable to impurity band formation. Our data shows that for hole concentrations larger than 1x10@super 19@ cm@super -3@, the lifetime decreases with the inverse cube of the hole density, which is indicative of a complex Auger process. The lifetime varied from about 1 ns at 1x10@super 19@ to 600 fs at 1x10@super@20 cm@super -3@. These data are compared to the theory of Takeshima and found to vary more steeply with p, even when the impurity-assisted and phonon-assisted processes are included. However, our data suggests that the latter two processes are active because of the doping dependence. These data suggest that the impurity band plays a critical role in carrier transport. The impact of the data on HBTs will be discussed.

Magnetic Interfaces and Nanostructures
Room 134/135 - Session MI-TuP

Emerging Materials & Nanostructures Poster Session

MI-TuP1 Structural, Electronic and Magnetic Properties of Chalcopyrite Magnetic Semiconductors: A First Principles Study*, **S. Picozzi,*** Univ. L'Aquila, Italy*; A. Continenza,* INFM - Univ. L'Aquila, Italy*; W.T. Geng, Y.J. Zhao, A.J. Freeman,* Northwestern University

Stimulated by recent experimental observations of room--temperature ferromagnetism of Mn@sub x@Cd@sub 1-x@GeP@sub 2@, we investigate the structural, electronic and magnetic properties of chalcopyrite systems as a function of Mn concentration by means of the first--principles density-functional-theory-based FLAPW (H.J.F.Jansen and A.J.Freeman, Phys. Rev. B 30, 561 (1984).) code. These new materials transcend the limitations (such as defect formation, and too low operating temperatures for spin injection and ferromagnetic properties) of the magnetic zinc-blende systems explored so far (e.g. Ga@sub x@Mn@sub 1-x@As) for spintronics applications. We investigate the effect of the anion (P vs As) and cation (Cd vs Zn) substitution in Mn-doped systems. Our calculations indicate that the antiferromagnetic alignment is the most stable ordering for the Mn-rich systems, at variance with that experimentally reported. Moreover, we focus on the dependence of the total magnetic moment per Mn atom and of the band gaps as a function of the Mn concentration in the different systems.

MI-TuP2 Component-resolved Electroluminescence from Spin-LED Structures: Implications for Quantifying Electrical Spin Injection in Semiconductors*, **B.T. Jonker**, A.T. Hanbicki, Y.D. Park, B.R. Bennett,* Naval Research Laboratory*; M. Furis, G. Kioseoglou, D. Coffey, A. Petrou,* State University of New York, Buffalo

The spin-polarized light emitting diode (spin-LED)@footnote 1@ has emerged as a very effective tool for accurately quantifying electrical spin injection in a model independent manner.@footnote 2@ The quantum selection rules which describe the radiative recombination process provide a direct and quantitative link between the circular polarization of the electroluminescence (EL) and the spin polarization of the electrically injected carriers. While these selection rules apply only to the free exciton and free carrier radiative recombination, the EL spectrum often consists of contributions from various recombination processes whose relative spectral weighting depends upon details of the LED heterostructure, such as doping, impurities and interface roughness. Common contributions include donor and acceptor-bound excitons, phonon replicas, and recombination mediated by various impurity levels or complexes. These components may completely dominate the spectrum in many instances. We resolve and identify such components in the EL spectra from several GaAs quantum well-based spin-LED structures by correlating reflectivity measurements with their dependence on doping, temperature and magnetic field, and examine the circular polarization of each. We show that these components exhibit markedly different polarizations which do not accurately reflect the electrical spin injection efficiency. Certain of these features derive from many-body effects, and may provide insight into related spin relaxation processes. We show that a reliable measure of spin injection efficiency can be obtained only if one takes care to spectroscopically resolve and accurately identify the origin of the components of the spin-LED EL spectrum. This work was supported by the DARPA SpinS program and ONR. . @FootnoteText@ @footnote 1@ B.T. Jonker, US patent # 5, 874,749 (filed 1993, issued 1999). @footnote 2@Fiederling, et al, Nature 402, 787 (1999), Jonker, et al. PRB 62, 8180 (2000), Park et al, APL 77, 3989 (2000).

MI-TuP3 Magnetic and Structural Properties of Fe- and Mn-Implanted SiC*, **N. Theodoropoulou**, A.F. Hebard,* University of Florida*; S.N.G. Chu,* Bell Laboratories, Lucent Technologies*; M.E. Overberg, C.R. Abernathy, S.J. Pearton,* University of Florida*; R.G. Wilson,* Consultant*; J.M. Zavada,* U. S. Army European Research Office, UK

P-type 6H-SiC substrates were implanted with Mn@super +@ or Fe@super +@ at doses of 3-5x10@super 16@ cm@super -2@ under conditions that avoided amorphization (substrate temperate ~350°C). After annealing at 700-1000°C, the magnetic properties of the samples were examined by SQUID magnetometry. The Mn-implanted SiC did not show any magnetization, remaining paramagnetic, but the Fe-implanted samples showed ferromagnetic properties below 200 K for the highest dose employed. The origin of the ferromagnetism is not the formation of secondary phases involving precipitation of the Fe. Results for Ni and Co implantation will also be presented, along with a comparison of data for implantation of the same elements into p-GaN epitaxial layers.

MI-TuP4 Magnetism and Transport in Manganite-based Trilayers A/B/A (A: La@sub 0.6@Sr@sub 0.4@MnO@sub 3@; B: La@sub 0.9@Sr@sub 0.1@MnO@sub 3@, La@sub 0.67@Ca@sub 0.33@MnO@sub 3@)*, **L.B. Steren**, M. Sirena, M. Granada, J. Guimpel,* Centro Atomico Bariloche and Instituto Balseiro, Argentina

We have studied the physical and structural properties of trilayers based on manganites compounds. Different ferromagnetic spacers, insulator (B1) and metallic (B2), have been used in order to compare the magnetotransport effect and interlayer coupling of both systems. Thin films and trilayers have been grown by dc sputtering. Films of La@sub 0.6@Sr@sub 0.4@MnO@sub 3@ ("A"}), La@sub 0.67@Ca@sub 0.33@MnO@sub 3@ ("B2") and La@sub 0.9@Sr@sub 0.1@MnO@sub 3@ (``B1"}) with thickness varying from 5nm to 50nm have been first prepared in order to study the intrinsic properties of these materials. "A" thin films are ferromagnetic with a Curie temperature around room temperature. These manganites present a metal-insulator transition below T@sub C@ and exhibit colossal magnetoresistance. A similar behaviour has been found in the "B2" films, with lower characteristic temperatures. "B1" are also ferromagnetic but present different transport properties : They are insulators between 4.2K and room temperature. All the compounds preserve its general properties, even for the smaller thicknesses. However, an important depression of the Curie point is observed as the films thickness is decreased. The trilayers have been prepared with different A and B thicknesses (10 nm <th@sub A@<50nm and 5 nm <th@sub B@< 15 nm). Strongly textured X-ray difraction patterns have been observed in the heterostructures. The magnetic coupling between A layers has been studied through temperature and field dependence of magnetization curves. Remanent magnetization curves show a single ferromagnetic transition around 200K. A metal-insulator transition is observed below the Curie point. Both results suggest a ferromagnetic coupling of the system. However, the role of the ferromagnetic spacer in the coupling cannot be explained by these measurements only. Complementary measurements of ferromagnetic resonance are under progress in order to better understand the interlayer coupling in these systems.

MI-TuP5 Observation of the Two-stage Magnetic Transition and the CMR Effect in Aged La@sub 0.5@Sr@sub 0.5@CoO@sub 3-@@delta@ Films Prepared by Laser Ablation*, **V.G. Prokhorov**,* Institut of Metal Physics, Ukraine*; J.S. Park, S.Y. Park, Y.P. Lee,* Hanyang University, Korea*; K.W. Kim,* Sunmoon University, Korea*; V.M. Ishchuk,* Insitute of Single Crystals, Ukraine*; I.N. Chukanova,* Institute of Single Crystals, Ukraine

The magnetic and transport investigations have been carried out for the as-deposited and the long-time aged La@sub 0.5@Sr@sub 0.5@CoO@sub 3-@@delta@ films prepared by pulsed laser deposition. It was shown that a decrease in the oxygen concenturation during aging of the film leads to the tetragonal distortion of the crystal lattice, to a shift of the metal-insulator transition temperature to a lower temperature(T@sub p@ = 250 K), and to the observation of a CMR effect (up to 3 % at magnetic field of 5 T). In addition to the usual ferromagnetic transition at T@sub c@ = 250 K, the second magnetic transition was observed at T@sub M@ = 50 K that is treated as the appearance of a cluster glass magnetic state. The non-monotonic behavior of the resistance observed in the low-temperature range, T < T@sub p@, is explained by the weak localization of the carriers.

MI-TuP8 Temperature Dependence of Line Width of Ferromagnetic Resonance in Nickel-Zinc Ferrites*, **S.C. Byeon**,* University of Alabama, US*; C. Alexander,* University of Alabama*; H.B. Hong, T.Y. Byun,* Seoul National University, Korea*; C.K. Kim,* Hanyang University, Korea*; K.S. Hong,* Seoul National University, Korea

The systematic temperature dependence in line width of ferromagnetic resonance with the Fe content was observed at X band (9.78GHz) in (Ni@sub 0.5@Zn@sub 0.5@)@sub 1-x@Fe@sub 2+x@O@sub 4@ (-0.2@<=@x@<=@0.2). The line width of the stoichiometric composition (x = 0) showed minimum value, 50 Oe. In contrast, the line width of the non-stoichiometric compositions sharply increased to 210 Oe with increasing non-stoichiometry (x). The mechanism for this line width broadening was investigated using thermoelectric power and electrical resistivity, since the contribution of anisotropy and porosity to the line width was negligible in this compositional region. In Fe excess region, Fe@super 2+@ ion concentration increased with increasing Fe content, resulting in line width broadening due to relaxation. But, it was suggested that Ni@super 3+@ and Fe@super 2+@ ions coexist in Fe deficient region. Therefore the increase of line width in nickel-zinc ferrites originated from the Fe@super 2+@/Fe@super 3+@ magnetic relaxation in Fe excess region, and the Fe@super 2+@/Fe@super 3+@, Ni@super 2+@/Ni@super 3+@ magnetic relaxation in Fe deficient region.

MI-TuP9 Magnetic Circuits for Atomic Matter Waves*, **M. Vengalattore**, W. Rooijakkers,* Harvard University*; S.A. Lee,* Colorado State University*; T. Deng, G.M. Whitesides, M. Prentiss,* Harvard University

Atom optics is an important branch of physics in which the quantum nature of atoms is exploited to realize systems equivalent to photonics. An example is the (single mode) atomic waveguide as compared to the (single mode) optical fiber. Another example is the atom laser, based on matter wave amplification, realized in 1997.@footnote 1@ The production of these matter waves, which are coherent over distances > 10 cm has facilitated applications such as interferometry. Since atoms have a much larger mass than electrons or photons, they offer the unique possibility of doing ultrasensitive gravitational field measurements. Furthermore, since the interactions can be controlled, neutral cold atoms provide a promising system for quantum computation. Following the integration in optics and electronics it makes sense to pursue miniaturization of atom-optical systems. This will allow for the realization of more complex functions on a relatively small surface. Arguably magnetic field gradients provide the most versatile means for non-dissipative manipulation of atoms. In this paper we describe a newly developed waveguide for coherent transport of atoms and possible future applications of this technology. Our waveguide consists of four parallel strips of ferromagnetic material, wound with kapton isolated wire. This configuration results in a magnetic field minimum above the surface. The position of this minimum can be controlled by varying the currents in the wires. Weak field seeking atoms can be trapped in this minimum by using laser cooling techniques, forming a magneto optical trap (MOT).@footnote 2@ Atoms from the background vapor are decelerated by laser beams and accumulate in the magnetic minimum. To provide damping in all directions the surface above the magnetic strips has been made reflective with a gold layer. In our experiment we use diode lasers with a wavelength of 852 nm to cool @super 133@Cesium atoms. The fluorescence of the atoms can be imaged onto a CCD camera. We have created very long (aspect ratio 1:500) and thin (20 mm) clouds. In our waveguide we obtain a gradient of 3 kG cm@super -1@ A@super -1@, and by further miniaturization we anticipate a further increase by a factor 10@super 3@. The next step is fabricating more complex structures. One example is the quantum point contact: a constriction through which the conductance of matter waves shows steps as a consequence of the quantum mechanics.@footnote 3@ Another example is a magnetic storage ring for atoms. Connecting up both ends of our waveguide seems a logical extension of our previous work. We are pursuing the propagation of matter waves in such a device, which may then be used as an interferometer for ultrasensitive inertial sensing. Presently we use mu-metal sheet to construct these devices. Alternatively we have also been using lithography@footnote 4@ and permalloy deposition. We continue our search for materials capable of generating large magnetic field gradients on a small substrate with the possibility of designing complex circuits for ultracold atoms. @FootnoteText@@footnote 1@M. Andrews, C. Townsend, H-J Miesner, D. Durfee, D. Kurn and W. Ketterle, Science 275, 637 (1997). @footnote 2@E. Raab, M. Prentiss, A. Cable, S. Chu and D.E. Pritchard, Phys. Rev. Lett. 48, 596 (1982). @footnote 3@J. H. Thywissen, R.M. Westervelt and M. Prentiss, Phys. Rev. Lett. 83, 3762 (1999). @footnote 4@N. H. Dekker, C. S. Lee, V. Lorent, J. H. Thywissen, S. P. Smith, M. Drndic, R. M. Westervelt and M. Prentiss, Phys. Rev. Lett. 84, 1124 (2000).

MI-TuP10 Investigation of MFM Tip Induced Magnetization Reversal of Magnetic Nanostructures*, **X. Zhu**, P. Grutter,* McGill University, Canada*; V. Metlushko,* University of Illinois at Chicago*; B. Ilic,* Cornell University

Magnetic Force Microscopy (MFM) has become a standard technique to study the magnetic reversal of nanoparticles. However, the magnetic tip stray field contribution to the reversal characteristics has not been systematically investigated. Here we compare data obtained in different operation modes of MFM such as tapping/lift mode or non-contact mode. We investigated e-beam patterned permalloy arrays with nominal thickness of 30nm, with aspect ratios of 1:1 up to 10:1, with widths of 100nm, 150nm and 200nm, and different spacing. Si cantilevers coated with 10nm to 90nm of CoPtCr, NiFe or NiCo are used as magnetic probes. Previously, we have found that the particle moment can easily be reversed when MFM measurements are performed in tapping and lift mode.@footnote 1@ This is associated with the fact that during tapping the tip stray field can be very substantial during part of the tip oscillation cycle. In the present study, we performed MFM measurements in the non-contact mode in our homebuilt vacuum MFM to further characterize how the magnetic tip influences the magnetic sample state. For large tip-sample separation (typically >100nm), and for large aspect ratio particles, we found that the magnetized tip very seldom reverses particle moments. These particles mainly form single domains due to their shape anisotropy. Within a few (

MI-TuP11 Magnetic Anisotropy in Epitaxial Fe(001) Micrometric Squares by Magneto Optical Torque*, D. Jaque,* Universidad Complutense de Madrid, Spain*; G. Armelles,* Instituto de Microelectrónica de Madrid, CNM-CSIC, Spain*; J.I. Martín,* Universidad de Oviedo, Spain*; P. García-Mochales, **J.L. Costa-Krämer**, F. Briones,* Instituto de Microelectrónica de Madrid, CNM-CSIC, Spain*; J.L. Vicent,* Universidad Complutense de Madrid, Spain

Magneto Optic (MO) studies are performed on regular arrays of 200 Å thick Fe (001) epitaxial tiles with different micrometric lateral sizes. MO studies are performed both on reflected and diffracted spots and analyzed in terms of the homogeneity of the magnetization within the tile. These are compared with predictions from micromagnetic simulations. The MO response to a rotating magnetic field (Magneto Optical Torque - MOT)is also measured in these structures, finding a clear evolution from the biaxial crystalline anisotropy towards an uniaxial one as the tile lateral size is reduced at constant thickness.

MI-TuP12 Annealing Effect on Structure and Magnetism of CoNi Pattern Quantum Dots*, **H.L. Li**, C.W. Wang, D.H. Qin, M.K. Li,* Lanzhou University, P. R. China

NiCo alloy nanowires were prepared by AC electrodeposition into self-assembled porous anodic alumina template. Then the sample was annealed at 500 °C, 6 hours, with argon as protected gas. The composition, microstructure and magnetism of samples used in this work were characterized by atom absorbed spectrum, transmission electron microscopy (TEM), scanning electron microscopy (SEM), x-ray diffraction (XRD), and vibrating sample magnetometer (VSM). XRD results showed that there were preferred orientation in CoNi nanowire arrays with Ni content range from 0.2 to 0.8 during electrodeposition, while random orientation was observed after the sample was heat-treated. Though the shape anisotropy was very high in the sample, it is found that the squareness (Mr/Ms) of the hysteresis of the samples (Ni content is in the range of 0.2 to 0.8) was only about 0.6 before annealing, and increased to about 0.9 after annealing. As its high bit density, such media may be used as high-density quantum magnetic disks. A qualitative discussion was given and explanation of reversal mechanism was offered in term of localized magnetization model.

MI-TuP13 Magnetic Coupling in Epitaxial Fe/MgO/Fe Arrays of Micro Tunnel Junctions*, **J.L. Costa-Kramer**, J.V. Anguita,* Instituto de Microelectronica de Madrid, CNM, CSIC, Spain*; J.I. Martin,* Universidad de Oviedo, Asturias, Spain*; C. Martinez-Boubeta, A. Cebollada, F. Briones,* Instituto de Microelectronica de Madrid, CNM, CSIC, Spain

The magnetic properties of planar 100 Fe/ x MgO / 100 Fe epitaxial ferromagnetic micro tunnel junction arrays have been measured for different lateral sizes of the junctions (1-50 Âµm) and barrier thicknesses; (x=10,20,50,70). When the top and bottom electrodes magnetizations are uncoupled, they orient antiparallel in zero field due to the magnetostatic energy gain. On the other hand, the two electrodes magnetizations orient parallel when direct exchange couples them effectively through the barrier, most probably due to a critical density of pinholes. We find that both, lateral size and barrier thickness influence the ratio of junctions with their electrodes magnetization antiparallel to those in which they orient parallel. For a given barrier thickness, there is a threshold below which mostly all of the junction electrodes couple antiparallel. This happens at about 4 Âµm lateral size for electrodes separated by a barrier of 10 MgO (close to only two MgO unit cells). The field ranges where these phenomena occur agree reasonably well with the predictions from a simple analytical model, in which we solve the energetic balance between magnetostatic energy gain and orientational energy loss for our Fe/MgO/Fe sandwich geometry. In addition, and comparing with our previous results with single layer Fe microtile arrays, we confirm the intuitive picture that the micro sandwich structures can be placed closer than the single layer structures before they interact magnetically with their closest neighbors. This is due to a preferred closure of the magnetic flux between top and bottom electrodes in the sandwich structure, reducing considerably the magnetic field at the closest neighbors positions.

Nanotubes: Science and Applications Topical Conference
Room 134/135 - Session NT-TuP

Poster Session

Moderator: M. Meyyappan, NASA Ames Research Center

NT-TuP1 Field Emission Microscopy Observation on Single-Walled Carbon Nanotubes with Atomic Resolution*, Z.X. Zhang, **G.M. Zhang**, M. Du, X.X. Jin, S.M. Hou, Z.J. Shi, Z.N. Gu, W.M. Liu, X.Y. Zhao, Z.Q. Xue,* Peking University, China

We assembled single-walled carbon nanotubes (SWCNs) onto tungsten carbide thin film on a tungsten tip surface, which was formed due to the segregation of carbon element in polycrystalline tungsten. Then by using Field-Emission Microscope (FEM) and quadrupole mass spectrometry, we respectively observed the field emission from the SWCNs and analyzed the components of the residual gas with the sample receiving heat treatment. The pattern of FEM image underwent obvious change as the heating temperature varied. The heat treatment at approximately 1000¡æ was found to result in the appearance of an FEM image with atomic resolution of an open-ended SWCN. The quadrupole mass spectrometry analysis showed the existence of carbon and oxygen atoms, which are believed to be released under high temperature from the spaces among the grains inside the polycrystalline tungsten. We think that these carbon and oxygen atoms imposed decoration upon the tube ends. Oxygen atoms reacted with amorphous carbon on the ends of the carbon nanotubes and generated CO and CO@sub 2@, which than escaped into vacuum. Carbon atoms might fill the defects so that relatively perfect structures resulted. We further believe that this kind of decoration led to the protrusion of an individual SWCN, which made the atomic resolution of FEM image possible.

NT-TuP2 Field Emission Properties of Carbon Nanotubes*, Z.Q. Xue*, *M. Du, J.P. Sun, H. Zhang, W.M. Liu, S.M. Hou, G.M. Zhang, Z.X. Zhang, Z.J. Shi, Z.N. Gu, L.M. Peng,* Peking University, China

SWCNTs have been synthesized and purified. Using a water colloid, SWCNTs have been assembled at the end of a tungsten tip that can be used as samples of field emission microscope (FEM) and field ion microscope (FIM). Images of a carbon nanotube open end were studied by the field ion microscope. Atomic resolution patterns of the tube open end were obtained. Field emission properties of SWCNTs have been studied exploiting the field emission microscope (FEM). A field emission pattern of an SWCNT at atomic resolution was observed, which was consistent with the calculated results of a (9,9) armchair SWCNT. Conventional field emission analysis utilizes the Fowler-Nordheim equation, a typical current versus voltage curve of SWCNT was measured. The plotting of ln(I/V @super 2@) versus 1/V shown yielded a straight line in agreement with the Fowler-Nordheim equation, confirming the current resulted from field emission.

NT-TuP4 Scanning Tunneling Microscopy of Single-walled Carbon Nanotubes with Metallo-phthalocyanine Adsorbates*, J. Lee,* Seoul National University, Korea*; J.-Y. Park,* Cornell University*; H.J. Kim,* ***H. Suh***, Seoul National University, Korea*; Y. Kuk,* Seoul National University, Korea, South Korea*; H. Kato, T. Okazaki, H. Shinohara,* Nagoya University, Japan

Since the existence of carbon nanotubes are first reported in early 1990s, efforts have been made to characterize the electronic, transport and mechanical properties of this new form of carbonaceous material in various situations with views to exploit them as building blocks of useful nanoscale devices or sensors. One of the major usefulness of nanotubes lies in the fact that the electronic and transport properties of a nanotube as a metal or a semiconductor are very sensitive to chemical adsorbates whose concentration can be well controlled and modulated after the creation of the nanotube. Therefore it is an intuitively natural idea to dope the nanotubes with functional molecules sensitive to a few specific chemical ligands or physical environments (light, temperature, etc) to use them as physical, chemical or biological sensors. In this report we present the results of recent STM studies on nanotubes with metallo-phthalocyanine (M-Pc) molecule adsorbates. M-Pc's are chosen because they are chemically stable up to the sublimation temperature, immobile at room temperature on most host surfaces and have different electronic sensitivities to various toxic gases. Atomic resolution images and spectroscopic data on and near the adsorbed single M-Pc will be presented.

NT-TuP5 In-situ Chemical Experiments in Carbon Nanotubes*, N.N. Naguib*, *Y. Gogotsi,* Drexel University*; J.A. Libera,* Northwestern University

Graphitic carbon nanotubes were synthesized by using a water-based mixture, such as equilibrated C-H-O fluid, in the presence of a catalyst, specifically Ni, at 700-800°C under 60-100 MPa pressure.@footnote 1,2@ TEM and electron diffraction analysis show that these carbon nanotubes are characterized by having high perfection of graphene layers, long and wide internal channels, Ni tips, and internal liquid inclusions trapped during the synthesis. During the growth of a tube, the synthesis fluid, which is a supercritical mixture of CO, CO@sub 2@, H@sub 2@O, H@sub 2@, and CH@sub 4@, exists inside the tube. After closure of the tube, aqueous liquid and gases are trapped inside. Closed hydrothermal nanotubes, unlike conventional nanotubes produced in vacuum or at ambient pressure, contain water and gases encapsulated under pressure. H@sub 2@O, CO and CH@sub 4@ are expected to dominate from thermodynamic calculations done using ChemSage 3.1 Gibbs energy minimization code. These nanotubes can be used as miniature pressure vessels for in-situ studies. Thus, they provide a unique opportunity for studying the behavior of fluids in nanosize channels, and for analysis of aqueous samples in TEM. The liquid inclusions were studied by using TEM, where apparent condensation and evaporation of liquid as well as a strong interaction between the liquid enclosed and the nanotube@super -@s walls were observed. These experiments demonstrate the possible use of nanotubes for in-situ study of carbon chemistry @FootnoteText@ @footnote 1@ Y.G. Gogotsi, M.Yoshimura, Nature 367, 628-630 (1994) and Y.G. Gogotsi, K.G. Nickel, Carbon 36, 937-942 (1998) @footnote 2@ Y.Gogotsi, J. Libera, and M. Yoshimura, J. Mater. Res., Vol. 15, No. 12, 2591-2594(2000)

NT-TuP7 Characteristic of Carbon Nanotube Tip in UHV-STM*, K. Ojima*, *M. Ishikawa, M. Yoshimura, K. Ueda,* Toyota Technological Institute, Japan

Recently much attention is paid to carbon nanotube (CNT) because of its unique structural and electric properties. Field emitter, nano-tweezers and probe in scanning probe microscopy are expected for future application using CNTs, and have been extensively studied. In terms of the last application, most of reports are devoted to in the fields of atomic force microscopy. However, there is few study to use CNT in scanning tunneling microscopy (STM). Here we report on the application of CNT for STM probes in ultrahigh vacuum in order to investigate its capability. CNTs are attached to the tungsten tip using a new preparation method we recently proposed [unpublished]. The presence of CNT at the apex of the tip is confirmed before and after the STM experiment by scanning electron microscope. Before STM measurement, the contamination on the tip is removed by radiant heating. The Si(100)2x1 surface is used as the reference specimen, as is prepared by conventional method. STM images of Si(100)2x1 surface using CNT tip reveal individual silicon atoms in dimer units. However the image is a little bit vaguer than the case without CNT. This is probably related to the electric property of CNT. In order to image the surface structure clearly, the sample bias voltage and the tunneling current should be set at larger than 1.5V and lower than 0.1nA, respectively, which is apparently different condition from the tungsten tip without CNT. It is also noted that in the images obtained by CNT, no ghost such as double tip effect is observed. The voltage dependence of STM images will be presented in order to clarify the electric property of the CNT tip.

NT-TuP8 Catalyst Effects in Its Deposition Rate and Kinds on Growth and Emission Characteristics of Carbon Nanotubes*, J.H. Han*, *S.H. Choi, T.Y. Lee, Y.W. Jin, J.E. Jung, J.B. Yoo, C.Y. Park,* Sungkyunkwan University, Korea*; H.J. Kim, Y.J. Park, I.T. Han, N.S. Lee, J.M. Kim,* Samsung Advanced Institute of Technology, Korea

Research on carbon nanotubes (CNTs) has been extensively carried out in past few years because of their own unique physical properties and their potential applications such as flat panel displays and vacuum microelectronics. In practical applications, a role of metal-catalyst has been very important for growth of CNTs in various synthesis methods. Among effects of metal-catalyst, an initial formation and various kinds of metal-catalyst film may have great effects on CNTs growth. Recently we observed that Ni film used as the catalyst-layer was differently formed according its deposition rate condition and thus CNTs were differently grown on it, hence this was systematically studied. Moreover, effects of a variety of metal-catalyst and buffer-metal on growth and emission characteristics of CNTs were investigated. In our experiments, the deposition rates of Ni film were varied from 1 Å/sec to 10 Å/sec. The metal-catalyst such as Ni, Co, Fe, Co-Fe and the buffer-metal such as Cr, Ti for improvement the adhesion between metal-catalyst and glass substrate were used. We have grown the vertically aligned CNTs on metal-catalyst coated glass with buffer-metal-layer at low temperatures below 550 °C by plasma enhanced chemical vapor deposition (PECVD). A DC plasma was employed, and C@sub 2@H@sub 2@ and NH@sub 3@ was used as a carbon source and a catalyst gas. We examined morphologies of CNTs using field emission scanning electron microscopy (FESEM). Microstructures of CNTs were investigated by high resolution transmission electron microscopy (HRTEM) and emission characteristics of CNTs were evaluated in vacuum chamber below 10@super -6@ Torr using phosphor-coated anode.

NT-TuP9 Conversion of Carbon Nanotube from Diamond-Like Carbon Films*, D. Sarangi*, *C. Godon, A. Granier, A. Goullet, G. Turban, O. Chauvet,* CNRS, France

A simple route to synthesize carbon nanotube (CNT) has been reported in this article. Vacuum annealing of diamond-like carbon (DLC) films, grown by microwave (MW - 2.45 GHz) excited electron cyclotron resonance (ECR) technique with a radio frequency (RF) bias applied to the substrate, mixed with catalyst in argon atmosphere leads to the formation of carbon nanotube. High-resolution transmission electron microscopy studies reveal highly graphitized multi-walled nanotubes (MWNT) or amorphous fibre like structures, depending on the catalyst amount. This synthesis process may give a new approach to understand the phase transition of different carbon allotropes into nanotube or nanostructure. @FootnoteText@ D. Sarangi's Present Address: Institut de Physique Experimentale, EPFL - Ecole Polytechnique Federale de Lausanne, CH-1015 Lausanne, Switzerland. C. Godon and O. Chauvet - Laboratoire de Physique Cristalline.

Plasma Science
Room 134/135 - Session PS-TuP
Plasma Deposition, Modeling, and Emerging Applications Poster Session

**PS-TuP1 A Comparitive Study of PECVD of Fluorocarbon Films Using C@sub 3@F@sub 8@ and C@sub 4@F@sub 8@ Precursors*, I.T. Martin,* *G. Malkov, E.R. Fisher,* Colorado State University

Plasma polymerization of fluorocarbons has been studied extensively. Recently, greater control over film characteristics has been attained through manipulation of plasma parameters, such as the formation of highly ordered CF@sub 2@ rich films using downstream continuous wave (CW) and pulsed hexafluoropropylene oxide (HFPO) plasmas. Here, we explore films deposited from the fluorocarbon precursors, octafluoropropane (C@sub 3@F@sub 8@) and octafluorocyclobutane (C@sub 4@F@sub 8@). These compounds are used industrially as alternatives to CF@sub 4@ and C@sub 2@F@sub 6@ in PECVD chamber cleans. Here, we characterize film properties as a function of input power, distance from the glow, and pulsed vs. CW conditions. Data from FTIR and XPS show films deposited with downstream CW and pulsed plasma conditions have higher CF@sub 2@ content and lower cross-linking with both precursors. However, films deposited with C@sub 4@F@sub 8@ plasmas have a lower mechanical flexibility than those deposited with C@sub 3@F@sub 8@ plasmas. Comparison to the HFPO system suggests the oxygen present in the HFPO system may be integral to the deposition of highly ordered films. In addition to film characterization, we have used our imaging of radicals interacting with surfaces (IRIS) method to measure the surface interactions of CF@sub 2@ radicals during plasma processing. CF@sub 2@ surface loss coefficients determined for 5-150 W C@sub 3@F@sub 8@ and C@sub 4@F@sub 8@ plasmas indicate relatively high levels of scattering in these systems (S>1). Scatter values greater than unity indicate CF@sub 2@ radicals are produced at the surface. Substrate biasing and ion removal techniques will be used to determine the effects of ions on these measurements. These data can be correlated with mass spectral data collected with the IRIS apparatus. Collectively, the data presented provide a comprehensive picture of these fluorocarbon systems, from the gas-phase to the material to the plasma-surface interface.

PS-TuP2 Spectroscopic Study of the Energetic Character of O@sub 2@/Ar/Tetramethyltin Discharge used for the Deposition of Transparent Conductive Tin Oxide Thin Films*, F. Arefi-Khonsari,* ENSCP-University of P.&M.Curie-Paris-France*; N. Bauduin,* ENSCP-University of P.&M.Curie-Paris-France, France*; J. Amouroux,* ENSCP-University of P.&M.Curie-Paris-France

Non stoichiometric tin oxide thin films have been deposited from an O@sub2@/Ar/tetramethyltin (TMT) mixture in a RF glow discharge parallel plate reactor at low pressure (15 Pa) and at low temperature (25-80 °C). The spectroscopic study of the discharge was performed with the help of optical emission spectroscopy and mass spectrometry. The aim of this work was to determine the role of the experimental parameters on the energetic and chemical characteristics of the discharge. This work was carried out by determining the vibrational temperature of N2 (C@sub 3@@PI@@sub u@,v'-B@sub 3@@PI@@sub g@,v" transition) as well as the rotational temperatures of OH (Q@sub 2@ rotational branch of the A@sub 2@@SIGMA@@super +@,v'=0 - X@sub 2@@PI@@sub i@,v'=0 transition) and N@sub 2@@super +@ (R0 rotational branch of the B@sub 2@@SIGMA@@sub u@@super +@, v'=0 - X@sub 2@@SIGMA@@sub g@@super +@,v'=0 transition). The mean electronic temperature was determined with the help of OES, by using Junk and Getty's model. In the latter they have used a maxwellian distribution of the EEDF which cannot hold in our conditions. That is why we have used the nonmaxwellian distribution of the energy of the electrons by solving the Boltzman's equation. The results show that the energetic character of the discharge was not modified when the organometallic precursor (i.e. TMT) was introduced. The dissociation rate increased with the power giving rise to a plateau around 200 watts which corresponded to the conditions where carbon free SnO@sub 2@ films were deposited. As for the biasing of the substrate electrode,which gave rise to an increase of the conductivity from 0.01 to 100 @ohm@@super -1@.cm@super -1@ with a decrease of the gap energy (from 3.5 to 2.5 eV), it did not give rise to a change of the energetic character. However, a spatially resolved study of the discharge by OES showed an increase of the intensities in the sheaths of both electrodes.

PS-TuP3 Spatial and Temporal Behaviour of the Plasma Parameters in a Pulsed Magnetron Discharge*, J.T. Gudmundsson,* University of Iceland, Iceland*; J. Alami, U. Helmersson,* Linkoping University, Sweden

We demonstrate the evolution of the electron energy distribution and the plasma parameters in a high density plasma in a pulsed magnetron discharge. The high density plasma is created by applying a high power pulse (1 -- 3 MW) with repetition frequency 50 Hz to a planar magnetron discharge. The spatial and the temporal behaviour of the plasma parameters are investigated using a Langmuir probe; the electron energy distribution function, the electron density and the average electron energy. Furthermore we report on the variation of the plasma parameters and electron energy distribution function with pulse length and the gas pressure in the pressure range 0.5 -- 5 mTorr. The electron density in the vicinity of the substrate, 20 cm below the cathode target, peaks at roughly 1 x 10@super 18@ m@super -3@ at 2 mTorr in a pulsed discharge with average power 300 W. Towards the end of the pulse two energy groups of electrons are present with a corresponding peak in average electron energy. With the disapperance of the high energy electron group the electron density peaks and the electron energy distribution appear to be Maxwellian like. Following the electron density peak the plasma becomes more Druyvesteyn like with higher average electron energy.

PS-TuP4 Evaluation and Measurement of Ionization Fraction in Ionized Physical Vapor Deposition using Parallel-plates Method*, K.-F. Chiu,* National Tsing Hua University, Taiwan*; Z.H. Barber,* University of Cambridge, UK*; R.E. Somekh,* Plasmon Data Systems Ltd., UK

The ionization fraction of the depositing flux of the ionized physical vapor deposition (IPVD) process was measured using a parallel-plates method. The method uses two parallel stainless steel plates forming a 1~2 mm slot, and measures the ionization fraction of the depositing flux travelling through the slot. A simple one-directional electric field was applied by biasing one side of the plates with the other side earthed. Negative bias was applied to avoid serious purperbation of the plasma. Since the ionized atoms are attractive to the biased side, the ionization fraction can be obtained by comparing the deposition rates with and without bias. This method was evaluated by modelling the trajectories of the depositing ions under the influence of the applied electric field.

PS-TuP5 ICP Source Designs with Azimuthal Field Symmetry Despite a Current Node*, S. Srinivasan,* *L.J. Overzet, M. Goeckner,* University of Texas at Dallas

Inductively coupled plasma source-coils can be modeled as transmission lines. The current characteristics across the transmission line are dependent on the terminating impedance and the constitutive parameters of the source. When the terminating impedance of the planar coil is different from the characteristic impedance, it results in standing waves. When the size of the planar coil exceeds one-quarter wavelength, the standing waves can produce a current node on the source coil. The location of the current node along the source coil is dependent on the frequency of operation and terminating impedance. These current nodes and the formation of standing waves along the source coil induce azimuthal asymmetry in the electric fields and bring about non-uniform power deposition in the plasma. We can change the geometry of the coil by making it three-dimensional with the adjacent loops of the source running in opposite directions to reduce azimuthal asymmetry and minimize the effect of a current node. The position of the current node along the three dimensional source affects the symmetry of the electric fields. The exact relationship between the field asymmetry and the position of the current node is being investigated. The field variations can be minimized by placing the current node on a loop that is pushed away from the dielectric window. The length of the three-dimensional source can also be adjusted to yield uniform fields and power deposition in the plasma. A three-dimensional source coil geometry can allow sufficient latitude for designing the direction in which the currents travel and to specify how far the different loops need to be from the dielectric window. We believe that the isolation of the node loop in the source is a key to obtaining azimuthal symmetry. Increasing the size of the source even to include multiple nodes would not be an issue then. This material is based in part upon work supported by the Texas Advanced Technology Program under Grant No. 009741-0081-1999.

PS-TuP6 Control of Dissociation by Different Dilution Gases for Plasma Processing*, **KJ Taylor,*** University of California, San Diego*; S.M. Yun,* Lam Research Corporation*; Y.J. Park,* Samsung Electronics Corporation*; G.R. Tynan,* University of California, San Diego

Electron temperature and electron density are modeled by using simple 0-d particle and power balance modeling and measured by Langmuir probe in pure He, Ar, and Xe plasmas. Trace amounts of oxygen gas is added to each of the inert gas plasma and dissociation of oxygen gas is studied by actinometry and by mass spectroscopy with various powers and various ratios of O2/inert gas. Reasonable agreement between these results and the neutral atomic oxygen density estimated using a simple model based on the measured electron density and temperature. Preliminary dissociation results using fluorocarbon will also be shown.

PS-TuP7 Comparative Study of N@sub 2@/CH@sub 4@ Plasmas in Active Discharges and in Flowing Afterglow Conditions*, **R. Hrach,*** Charles University, Czech Republic*; J.C. Legrand, A.M. Diamy,* Universite Pierre et Marie Curie, France*; V. Hrachova, M. Vicher,* Charles University, Czech Republic

Methane is widely used in plasma processing. Experimental techniques used for the decomposition of methane into simpler hydrocarbons can be divided into two groups - processing in active discharges and processing in flowing afterglow conditions. While the first group of discharges can lead to preparation of solid products, the lower energies in afterglows are much more convenient for efficient gaseous chemistry. The aim of this contribution is to give an insight into the basic mechanisms leading to decomposition of methane and preparation of both solid and gaseous stable products in various experimental conditions. Therefore, a computer experiment describing the N@sub 2@/CH@sub 4@ plasma was prepared and both the common features and differences of methane decomposition in various types of discharges were discussed. Models consisted of reactions between neutral, charged and excited species. Input data were derived from Langmuir probe measurements and from emission optical spectroscopy. For the solution a macroscopic kinetic approach based on balance equations of individual species was used. In order to reduce the resulting models (consisting of more than 300 and 166 reactions - in active discharges and in flowing afterglow conditions, respectively) a method of reduction of the kinetic scheme was applied. In the discussion the fluxes of carbon and nitrogen atoms were studied in the dependence on concrete experimental conditions and an attention was devoted both to the methodology of simulation and to the reduction technique in plasma chemistry.

PS-TuP8 Diagnostics and Modelling of Ar/O@sub 2@ Plasma used for Plasma Oxidation of Al*, J. Pavlik, **S. Novak**, Z. Stryhal,* J. E. Purkyne University, Czech Republic*; R. Hrach, V. Hrachova, M. Vicher,* Charles University, Czech Republic

Plasma oxidation, utilising highly activated particles in oxygen or oxygen/argon plasma, is one of the low temperature techniques used to growth of dielectric films on metal and semiconductor surfaces. The contribution deals with a comparative study of plasma characteristics and thin oxide film properties with following tasks: to better understand the mechanism of plasma oxidation of aluminium thin films, to find basic factors which play a dominant role in the process studied, and to find factors which determine properties of the created oxide layers. The experiments were carried out in a system for plasma-chemical surface modification of thin films. A DC discharge was applied in an oxygen-argon mixture. The main diagnostic techniques applied in order to determine plasma parameters were the optical emission spectroscopy and the quadrupole mass spectrometry. Both the composition and the atomic surface density of prepared samples were studied by conventional Rutherford elastic back-scattering. Investigation of morphology of the sample surfaces and surface roughness of the alumina thin film were performed by Atomic Force Microscopy. The experimental techniques are combined with computer experiment in order to achieve better insight into the problem solved. The computer experiment consists of several stages - model of gaseous plasma chemistry, model of the plasma-solid interaction, and model of processes on the surface of growing oxide film. The technique used was both the macroscopic kinetic approach and combination of various simulation methods - fluid modelling and PIC-MC modelling.

PS-TuP9 Simulation of High Aspect Ratio Trench Profiles in Silicon under a SF@sub 6@/O@sub 2@ Plasma Chemistry by a 2D Surface Model Based on Monte-Carlo Techniques*, **G. Marcos,*** GREMI, CNRS-Universite d'Orleans, France*; A. Rhallabi,* LPCM, IMN, CNRS-Universite de Nantes, France*; P. Ranson,* GREMI, CNRS-Universite d'Orleans, France

Deep etching to obtain high aspect ratio trenches (deep/width >20) is a current challenge in view of new microelectronic applications. This objective needs a precise control of feature profile evolution during etching, which requires fine comprehension of surface mechanisms occurring. In order to understand consequences on the final etch profile effects due to reactive species in a high density SF6/O2 plasma, we have developed a two dimensional etching model. The species included are fluorine and oxygen radicals and ions which we study the interactions with silicon and mask (SiO2) surface. Angular and energetic distributions of ions are taken into account and calculated using Monte-Carlo simulation of ion transport across rf discharges sheaths. We assume that angular neutral distribution is isotropic. The surface model is based on Monte-Carlo approach allowing move the etched silicon surface by probabilistic criteria. It includes processes such as adsorption/desorption, chemically etching, passivation layer formation, ion preferential sputtering and reflexion, redeposition. The kinetic parameters are introduced as input data using experimentally performed measurements. The silicon area is discretized by a grid and each cell represents really a number of silicon sites. The simulation results show the increase in anisotropy of the etch profile with increasing the ion to neutral flux ratio. Undercut is due to spontaneous etching caused by the isotropic neutral flux. Ion angular distribution and mask geometry appear to be important parameters in the bowing formation. Formation and growth mechanisms of the passivation layer SiOxFy are now known with more accuracy, in function with certain parameters as surface temperature or ion distributions. Its consequences on the final trench topography is also studied.

PS-TuP10 Scalability of Innovative ICP Source Geometries*, **L.J. Pratti**, J.M. Marquis, M. Goeckner, L.J. Overzet,* University of Texas at Dallas

As industry moves towards plasma processing on larger substrates, there is a need for larger plasma sources. Due to transmission line effects, large traditional planar ICP sources produce non-uniform plasmas, and thus non-uniform processing rates across the substrate. Recently, a three-dimensional coil geometry which can reduce these non-uniformities was introduced.@footnote 1@ In this paper, we examine standing wave effects on the field intensities and uniformities when a current node is present on the planar and various 3-D coils. Preliminary experiments show uniformity improves by a factor of 3 or more using the 3-D coil. The location of the node on the coil is found using a dynamic current probe. The field measurements are made with a B-dot probe in the absence of plasma. A separate paper presents the results of a predictive model of the system. @FootnoteText@ This material is based in part upon work supported by the Texas Advanced Technology Program under Grant No. 009741-0081-1999. @footnote 1@M. H. Khater, L. J. Overzet, Plasma Sources Sci. Technol. 9 (2000) 545-561.

PS-TuP11 Study of Pulsed Plasma Doping by Experimental Diagnostics and HPEM Simulations*, **Y. Lei**, E.A. Oakes, M. Goeckner,* University of Texas at Dallas*; S.B. Felch, Z. Fang, B.-W. Koo,* Varian Semiconductor Equipment Associates

Pulsed plasma doping is a potential solution to implement ultra-shallow junctions. Previous studies of the pulsed plasma doping process have closely examined the implanted species@footnote 1@ and device characteristics.@footnote 2@ In this paper we examine fundamental issues related to the plasma source used in that process. The work reported here combines both experimental and theoretical studies. Experimental work consists primarily of Langmuir probe studies of the discharge. Early data indicate that during a 20 µs long implant pulse the plasma density is on the order of 10@super 9@ cm@super -3@ and the electron temperature is ~2 eV. Between pulses, the density falls to 10@super 6@ cm@super -3@ and the electron temperature collapses to ~0.2 eV. We combine the experimental work with simulations using the Hybrid Plasma Equipment Model, HPEM.@footnote 3@ Comparisons will be made between the simulation and the experimental results. Finally, we will discuss likely electron heating mechanisms in this discharge. @FootnoteText@ @footnote 1@M.J. Goeckner, S.B. Felch, Z. Fang, et al. "Plasma doping for shallow junctions," J VAC SCI TECHNOL B 17: (5) 2290-2293 SEP-OCT 1999 @footnote 2@ D. Lenoble, M.J. Goeckner, S.B. Felch, Z. Fang, J. Galvier and A. Grouillet, "Evaluation of Plasma Doping for sub-0.18 µm Devices" Proceedings of the 12th International Conference on Ion implantation Technology '98, Kyoto, Jp, June 22-26, 1998. @footnote 3@

R. Kinder and M. J. Kushner, "Wave Propagation and Power Deposition in Magnetically Enhanced Inductively Coupled and Helicon Plasma Sources", J. Vac. Sci. Technol. A 19, 76 (2001). The authors from UTD gratefully acknowledge M.J. Kushner for allowing us to use HPEM in this study. This work is supported by Varian Semiconductor Equipment Associates.

PS-TuP12 Neutral Gas Pressure and Flow in High Density Plasmas*, **M.A. Nierode**, D.B. Graves,* University of California at Berkeley

The charged species in high density plasmas often couple with the transport processes occurring in the neutral gas. The charged species in the plasma exchange mass, momentum and energy with the neutral species, and under some conditions this can have a profound impact on the neutral processes. We present model results of a neutral gas interacting with a high density plasma. Conservation equations for the neutral species are solved, decoupled from a plasma model, so that the plasma influences the neutral species as specified source terms in the appropriate neutral transport equations. We have included plasma heating, dissociation, and momentum exchange, with the assumed model of a diatomic neutral gas. In particular, we present results for the case of a plasma filling a tube through which a neutral gas flows. Plasma heating and molecular dissociation can have a significant effect on the gas mass-averaged velocity and therefore on the pressure drop in the tube. Depending on how the gas is introduced and pumped, the net effects may differ. In geometries in which gas flow can bypass the region of intense plasma, the effects can be very different. Principles for analyzing various cases are presented.

PS-TuP14 Numerical Optimization of a C@sub 4@F@sub 8@ Chamber Clean Recipe*, **G.I. Font**,* Kinema Research, US*; B. Devulapalli,* Fluent, Inc., US*; W.L. Morgan,* Kinema Research, US

Plasma deposition reactors are regularly subjected to non-value added cleaning schedules to eliminate build up inside the reactor. Cleaning minimizes flaking and particle shedding which can contaminate or destroy the integrated circuits being created on the wafer. If the cleaning step can be made as fast as possible, the down time for the tool can be minimized. Recently much effort has been devoted to the optimization of plasma reactor clean recipes. The criteria for optimization vary from clean time and expense of feed gas to environmental emissions of PFC's. Parameters which are usually considered for optimization include total gas feed rate, pressure, and mixture ratios of feed gasses. Optimizing studies require costly and time consuming experimentation. If the studies could be conducted numerically, the expense would be greatly reduced. The optimum point could also be tailored for specific reactor geometries. In this work, we use computational methods to optimize a C4F8 chamber clean chemistry. Comparison with experimental results shed light on the viability of conducting such optimizations numerically and give a unique perspective on the change in plasma constituents as the process parameters are varied.

PS-TuP16 Computer Modeling as a Tool to Design Non-Critical High Rate Deposition Conditions for the "Baffled Target" Reactive Sputtering Process*, **T. Nyberg**, F. Engelmark, J. Westlinder, S. Berg,* Uppsala University, Sweden

Normally it is quite puzzling to operate the target in the high rate metallic mode during reactive sputter deposition. To decrease the target poisoning, several authors have suggested to enclose the target into a box having a front aperture allowing sputtered material to be deposited through the aperture onto the substrates in the main chamber. The purpose of this box is to separate the reactive gas in the chamber from the target thereby decreasing the target poisoning. Non of the previous investigators, however, have made a detailed analysis of the full potential of this novel process design. By basically applying "Bergs´ model" for the reactive sputtering process to the conditions valid for this process we successfully were able to predict details of the behavior of the process. Most surprisingly we found out that with this "baffled target" it may be possible to carry out a perfect oxide deposition for a gas supply level even below the supply levels defining the hysteresis region. We have never observed such a favorable behavior for any type of reactive sputtering process before. This behavior offers extremely non-critical processing control allowing non-poisoned target high rate perfect oxide deposition. All our experimental results nicely correlates with the behavior predicted by the computer simulations.

PS-TuP17 Influence of High Power Densities on the Composition of Pulsed Magnetron Plasmas*, **A.P. Ehiasarian**,* Sheffield-Hallam University, UK, United Kingdom*; K.M. Macak, R. New, W.-D. Münz,* Sheffield-Hallam University, UK*; U. Helmersson,* Linköping University, Sweden

The application of high power pulses with peak voltage of -2 kV and peak power density of 3 kW.cm@super -2@ to magnetron plasma sources is a new development in sputtering technology. This study presents evidence of multiply charged Cr and Ti metal ions in the dense plasma region of the high power pulsed magnetron discharge and a substantially increased metal ion production compared to continuous magnetron sputtering. The average degree of ionisation obtained from growth rate measurements of the Cr metal flux generated in the plasma source was 30 % at a distance of 50 cm. The high power is applied to ordinary magnetron cathodes in pulses with short duration of typically some tens of microseconds in order to avoid a glow-to-arc transition. An Ar pressure of typically 0.4 Pa (3 mTorr) is maintained during the discharge. The time evolution within a pulse of the optical emission from Ar@super 0@, Cr@super 0@, Cr@super 1+@, and Cr@super 2+@ showed that at low power (0.2 kW.cm@super -2@) Cr and Ar excitation develops simultaneously. At higher powers (3 kW.cm@super -2@) a distinct transition from Ar to Cr plasma within the duration of the pulse was observed. Optical emission from the various species in the plasma showed an increase in metal ion-to-neutral ratio with increasing power. These observations indicate that a threshold plasma density exists when a transition from conventional pulsed sputtering to pulsed self-sputtering (similar to cathodic arc spots) occurs. First attempts to model the time-dependence of the OES signals are discussed.

PS-TuP20 Self-consistent Particle Modelling of Plasma-solid Interaction: Sheath Formation in Electronegative Plasma*, R. Hrach, **V. Hrachova**, M. Vicher,* Charles University, Czech Republic

Low-temperature reactive plasmas employing electronegative gases are often used for various material processing. Negative ions in such plasmas affect the transport of charged species from plasma to immersed substrates and in this way the corresponding plasma-chemical technologies. The same situation holds for probe diagnostics of low-temperature plasmas containing negative ions. The derived results depend on various plasma and electrode parameters - as plasma composition, pressure, and form of substrate/probe, etc. - in rather complicated way. In order to simplify the discussion of experimental results a PIC-MC plasma model was suggested and following questions were studied: * the influence of plasma composition, especially the influence of negative ions, on the distribution of electric potential near the metal substrate * the influence of pressure on the energy and angular distributions of charged particles in the vicinity of plasma-solid boundary as well as on the fluxes of charged particles on the substrate of solids immersed into plasma * the dynamical processes taking part in plasma-solid interaction when applying either negative or positive step voltages on the substrate. The simulation was performed for O@sub 2@/Ar plasma in the positive column of dc glow discharge. The attention was devoted both to the calculation of plasma properties together with their comparison with experimentally derived results and to the technique of computer simulation. Computer experiment enabled to discuss various mechanisms in the plasma affecting the distribution of electric potential as well as the fluxes of charged species separately.

PS-TuP21 A New Protective Layer Using Plasma Polymerized Thin Films in Plasma Display Panel*, **S.O. Kim**,* University of Illinois at Urbana-Champaign, South Korea*; G.H. Miley,* University of Illinois at Urbana-Champaign

Flat panel displays have recently received much attention in research and development as alternatives to cathode ray tube(CRT). The plasma display panel(PDP) is considered a promising candidate as a conventional display. The performance of ac-plasma display panel(PDP) is influenced strongly by the surface plasma characteristics on the protective layer. The new protective layer in ac-plasma display panel(PDP) manufactured by plasma polymerization is a monomer produced by MMA(Methyl methacrylate). The functional groups of MMA appeard in the PPMMA(Plasma polymerized methyl methacrylate) as well, and this was confirmed through an analysis using FT-IR. The polymerization rate of plasma polymer increased as a function of the plasma power and decreased as a function of the system pressure using scanning electron microscopy(SEM). Plasma polymer has highly secondary electron emission coefficient from 0.02 to 0.14 as a function of the pure Ne ions under accelerating voltage ranged from 50 V to 150 V.

PS-TuP22 Synthesis of Organic Polymer Thin Films by Plasma Assisted CVD for Low k Dielectrics Application*, M.-C. Kim,* ***S.-H. Cho****, J.G. Han, S.-B. Lee, J.-H. Boo,* Sungkyunkwan University, Korea

Plasma polymerized thin films have been deposited on Si(100) substrates at growth temperature between room temperature and 400 °C using thiophene (C@sub 4@H@sub 4@S) precursor by plasma assisted chemical vapor deposition (PACVD) method for low-dielectric device application. In order to compare physical properties of the as-grown thin films, the effects of the plasma power, gas flow ratio and deposition temperature on the dielectric constant and thermal stability were mainly studied. XRD and TED studies revealed that the as-grown thin films have highly oriented amorphous polymer structure. XPS data showed that the polymerized thin films that grown under different RF power and deposition temperature as well as different gas ratio of Ar:H@sub 2@ have different stoichiometric ratio of C and S compared with that of monomer, indicating a formation of mixture polymers. Moreover, we also realized that oxygen free and thermally stable polymer thin films could be grown at even 400 °C. The results of SEM, AFM and TEM showed that the polymer films with smooth surface and sharp interface could be grown under various deposition conditions. From the electrical property measurements such as I-V and C-V characteristics, the minimum dielectric constant and the best leakage current were obtained to be about 3.22 and 10 @super -11@ A/cm @super 2@, respectively.

PS-TuP23 Improved Gas-mixtures for High Efficiency in AC Plasma Display Panel*,* ***M.-P. Park****, T.-W Kim, H.-J. Hwang,* Chung-Ang University, Korea

In this work, we have examined the Ne-He-Xe gas discharge characteristics in the Plasma Display Panel (PDP) and explained the luminous efficiency at the various gas mixtures. The gas mixtures adopted to the PDP is necessary for both decreasing the power consumption and increasing the luminance efficiency. Therefore, for improving the luminous efficiency significantly in ac PDP, we suggest a new gas-mixtures; (Ne:He=7:3)-(~10%Xe) to achieve good performance for driving waveform as the function of gas pressure, Xe mixing ratio, Ne to He mixture, etc. In addition, the results of experimental measurements have been compared with those calculated by two-dimensional FDTD (Finite Difference Time-Domain method) model of the discharge, which is newly applied to our computer code. Through these results, we have found that He mixing ratio and gas pressure led to the decreasing of the delay time and increasing of the luminance efficiency, as Xe gas ratio increases.

PS-TuP24 The Effect of Washing Treatments on the Surface Chemistry of Plasma Coated Textiles as Studied by High Resolution XPS*, S.R. Coulson,* Dera, UK*; S.J. Hutton,* ***C. Moffitt,*** Kratos Analytical, UK

Hydrophobic and oleophobic repellency are highly desirable properties for textiles. Such behaviour can be imparted by coating the surface with perfluoroalkyl polymers. One method of applying such coatings is by plasma polymerisation.@footnote 1@ The advantages of such a solventless method are many and include reduction in waste, low process temperatures and a wide range of suitable substrate materials. However, one problem associated with fluorinated coatings applied to textlies is the loss of liquid repellency during washing. This is attributed to the rearrangement of the fluorinated surface molecules. Here we describe the surface chemistry, as studied by high resolution XPS, of a pulsed plasma deposited fluorinated acrylate before and after washing cycles. @FootnoteText@ @footnote 1@ H. Yasuda, Plasma Polymerisation, Academic Press, London, 1985.

PS-TuP25 Surface Reactions of Polyethylene with Nitrogen Plasmas/Ion Beams*,* ***A.J. Wagner****, S.R. Carlo, C. Vecitis,* Johns Hopkins University*; F. Reniers,* Universite Libre de Bruxelles, Belgium*; H. Fairbrother,* Johns Hopkins University

Nitrogen containing functionalities are often introduced into polymer surfaces to improve interfacial properties such as adhesion and biocompatibility. The process of nitrogenation at the molecular level has been probed by investigating the reactivity of polyethylene (PE) with N@sub2@@super+@ ions and N@sub2@ plasmas using X-ray Photoelectron Spectroscopy (XPS), Attenuated Total Reflectance (ATR), Atomic Force Microscopy (AFM) and contact angle measurements. XPS and ATR results indicate that a variety of different nitrogen groups are introduced during the interaction of nitrogen ion beams with PE, notably C-N, C=N, and CN moieties. These chemical modifications are also accompanied by changes in the surface roughness and frictional properties of the interface, as characterized by AFM. These results will be compared with related experiments carried out to determine the change in surface composition of PE as a result of nitrogen plasma and radical treatments. Titanium atoms have been deposited onto nitrogen modified PE interfaces by physical vapor deposition as a model for an industrial metallization process. The subsequent reactivity of the nitrogenated interfaces with titanium atoms will be discussed in terms of the formation of nitride and carbide species within the interfacial region. To further isolate the reactivity of specific functional groups in bulk polymeric substrates, results will also be presented on the reactivity of a CN terminated self-assembled monolayer with vapor phase titanium atoms.

PS-TuP26 Plasma, Electrochemical and Thermal Oxidations of Metals and Alloys as Methods for Designing Nanostructured Oxide Films*,* ***J.R. Parga,*** Instituto Tec. de Saltillo, Mexico*; M.A. Hossain,* Lamar University*; H. McWhinney,* Prairie View A&M University*; D. Mencer,* Penn State University*; D.L. Cocke,* Lamar University

Plasma, electrochemical and thermal oxidations of metals and alloys are methods of producing functional thin films. However, the fundamental physical chemistry of the film oxidation growth processes have not been sufficiently known to allow design of multicomponent oxide layers. Our reseach has recently determined the factors that control the development of oxide films on metals and alloys by thermal and electrochemical methods from which a predictive model has been developed. We have recently found that plasma methods are quite unique in producing oxide film structures that are not expected from these models. The uniqueness of the plasma method provides an alternative preparation that complements the thermal and electrochemical approaches. Our recent results using various metals and alloys such as Cu, Ni, Al, Zr, Ti and their binary and ternary alloys will be used to delineate the advantages and disadvantages of the three preparation methods and highlight the unique attributes of the plasma oxidation method. Various surface and subsurface characterization techniques have been used to structurally and chemically characterize the resulting films allowing insight into the reasons for the unique behavior of the plasma oxidation. The theoretical background and reaction models which allow structural design at the nanoscale for thermal and electrochemical oxidation will be used to examine the plasma oxidation processes and explore the the predictibility required for oxide film design at the nanoscale.

PS-TuP27 Change of Surfaces of PDP Panel during Discharge*,* ***K.H. Lee****, H. Soh, Y.C. Kim,* Hanyang University, Korea

Plasma display panel (PDP) is a most promising candidate for large-area wall-hanging displays because of the features of a simple panel structure and simple processes appropriate for large-area displays.@footnote 1@ Aging process accomplished for 48 hours in PDP fabrication stabilizes the inside of panel and maintains optical performance by initial discharge. We must reduce long aging time for productivity improvement. For these reasons, we investigated an effect which aging process exerts in surface of front panel and rear panel. In this experiment, we developed in-situ analysis system analyzing panel surface without the exposure to minimize the outside influence. This in- situ analysis system can analyze 7 inch test panel. The performance and lifetime of a PDP is strongly related to the MgO protection film, the phosphor layer and discharge gas.@footnote 2@ Therefore, we observed MgO protection film of front panel and Phosphor layer of rear panel according to aging time. Also, in order to find out surface changes according to plasma discharge, 30 minutes aging sample was discharged by He plasma with increasing power. The physical and chemical properties were characterized X-ray photoelectron spectroscopy (XPS), Auger electron microscopy (AES), Atomic force microscope (AFM), Mass spectroscopy (QMS200). @FootnoteText@ @footnote 1@Tsutae Shinoda,Masayuki Wakitani,Toshiyuko Nanto,Noriyuki Awaji and Shinji Kanagu IEEE TRANSATIONS ON ELECTRON DEVICE, vol.47,NO.1, 77 January 2000 @footnote 2@Kunio YOSHIDA, Heiju UCHIKE, Masahiro SAWA, IEICE TRANS.ELECTRON, VOL.E82-C, N10, 1798 (1999)

PS-TuP28 Characteristics of Capillary Electrode Atmospheric Pressure Glow Discharge and Its Application to Glass Substrate Cleaning*,* ***Y.H. Lee****, C.H. Yi, M.J. Chung, G.Y. Yeom,* Sungkyunkwan University, Korea

In this study, the characteristics of atmospheric low temperature plasmas generated by capillary electrodes were investigated for the application of the TFT-LCD glass substrate cleaning process. The characteristics of the plasmas were studied as a function of capillary aspect ratios, input power, electrode distance, the gas mixtures of He, O@sub 2@, Ar, and N@sub 2@, etc. using a high voltage probe, a current probe, Quadrupole Mass Spectroscopy (QMS), and optical emission spectroscopy (OES). The voltage between the electrodes increased with the increase of input power, the increase of electrode distance, the decrease of He flow rate, and the increase of O@sub 2@ flow rate. The increase of the voltage has led to unstable filamentary discharge from the stable capillary discharge. The use of capillary electrode instead of dielectric barrier electrode (the electrode covered with a non-capillary dielectric) not only decreased the electrode voltage, therefore, increased the stability of the plasma but also increased the discharge current and, therefore, the intensity of the plasma. Increased ionization and dissociation of the plasma species could be observed by OES with the increase of input power in He/O@sub 2@ mixtures. However, with the increase of O@sub 2@ flow rate in a constant He flow rate, the emission peaks from He decreased due to the increased electron consumption by oxygen while the emission peaks from O@sub 2@@super +@ and O increased due to the increased ionization and dissociation rates with the increase of oxygen concentration in the He/O@sub 2@ gas mixtures. Also, using He/O@sub 2@ gas mixtures, organic materials such as photoresist on the glass substrate could be successfully removed with the average etch rates higher than 570 nm/min.

PS-TuP29 The Relationship between Plasma States and Film Formation Behavior in Ti-Me-N by Double Magnetron Sputtering*, Y.M. Kim, J. Kim,* Sungkyunkwan University, Korea, South Korea*; J.G. Han,* Sungkyunkwan University, Korea

The main problems related to a DC reactive sputtering are instability process and low deposition rate. In recent years, in order to overcome these disadvantages, pulsed reactive unbalanced or dual magnetron sputtering is widely used for thin film deposition, such as insulating nitrides and oxides films. In general, for analysis of the influence of plasma parameters on physical properties of thin films, plasma diagnostics have been widely used. In previous works, Ti-N was deposited by unbalanced magnetron sputtering. We have measured plasma parameters during deposition of Ti-N by Langmuir probe and Optical Emission Spectroscopy (OES). As increasing discharge power, plasma density and electron temperature were increased the other side, plasma potential was decreased. In this study, we have developed the mid-frequency powered double magnetron sputtering system with two different material targets. We synthesized Ti-Me-N films with various doped metal contents in this system and analyzed microstructures of the sample with XRD and SEM. Also, for feedback control and analysis of the influence of plasma parameters, we have studied the relationship between plasma states and film formation behavior for double magnetron discharge conditions by Langmuir probe and OES.

PS-TuP30 Amorphous Metal-organic Chemical Vapor Deposition Nb@sub x@Ta@sub (1-x)@N Films for Diffusion Barrier*, W.C. Gau, C.W. Wu,* National Tsing Hua University, Taiwan, R.O.C.*; T.C. Chang,* National Sun Yat-Sen University, Taiwan, R.O.C.*; C.H. Li,* National Chiao Tung University, Taiwan, R.O.C.*; C.J. Chu, C.H. Chen,* Nanmat Technology Co., LTD., Taiwan, R.O.C.*; L.J. Chen,* National Tsing Hua University, Taiwan, R.O.C.

To incorporate Cu into interconnection structures, it is necessary to introduce diffusion barrier to prevent Cu from entering the silicon substrate and to form deep level traps. The presence of grain boundaries in the film is generally detrimental to the diffusion barrier properties. One way to eliminate grain boundaries is to render the barrier structure amorphous. In the present work, the resistivity, composition, crystal structure, and microstructure of Nb@sub x@Ta(@sub (1-x)@N film were investigated. Amorphous diffusion barrier of Nb@sub x@Ta@sub (1-x)@N films were deposited in a CVD system with mixed precursors (75% NB=(Net@sub 2@)@sub 4@ and 25% (Net@sub 2@)@sub 3@Ta=NEt) and NH@sub 3@ gas. The Nb@sub x@Ta@sub (1-x)@N films were deposited at substrate temperatures of 375-500 °C, reactor working pressures of 0.3-0.5 Torr, Argon carrier flow rate of 10 sccm, ammonia reactant flow rates between 5 and 30 sccm. The thermal stability was evaluated by electrical measurement. In addition, the barrier films were deposited onto patterned wafer with 0.2 µm-contact holes to check the step coverage. The effects of N@sub 2@/H@sub 2@/NH@sub 3@ gaseous plasma (200W) post-treatment with various times (3-10 min) were also investigated. The films were subsequently characterized by transmission electron microscopy (TEM). Depth profile and the chemical environment of elements in the films were analyzed by x-ray photoelectron spectroscopy (XPS). The amorphous Nb@sub x@Ta@sub (1-x)@N films were found to contain a low C concentration (10%), high N concentration (40%), and low resistivity with NH@sub 3@ as a reactant gas. The resistivity of barrier was increased with time owing to the absorption of oxygen in the atmosphere. NH@sub 3@ plasma post-treatment for 3 min was found to be effective in preventing the oxidation and reducing the resistivity. The Nb@sub x@Ta@sub (1-x)@N films were found to be an effective barrier up to 550 °C for 30 min.

PS-TuP31 Silicon Trench Oxidation Layer Formation by Employing Oxygen Negative Ion*, **H. Shindo,*** Tokai University, Japan

A low temperature and low damage silicon oxidation technique has been highly required in various ULSI processes. In particular for trench isolation of a memory cell to realize further integrations, the oxidation should be ion-assisted for directionality but with low damage. The objective of this work is to study silicon trench oxidation by negative oxygen ion to form an insulation layer for cell isolation. The plasma was produced in a 6 inch stainless-steel chamber, and the downstream plasma was mainly considered because in this region the negative ion was highly populated. Silicon oxidation was made in downstream region, and the stage was biased by the DC voltage as well as the RF bias to irradiate both negative and positive ions. The RF bias voltage was applied to the stage with a cored-transformer, and the secondary of the transformer was biased by DC voltage at the same time. The oxidation experiment was performed at the substrate temperature of 100 to 200 degree C. The frequency of the bias was varied with keeping the RF voltage of 65 V peak-to-peak.The oxidation depth strongly depended on the frequency and there was a limitation of oxidation at both sides of frequency. Since the limitation begins at about 1 MHz which is close to the negative ion plasma frequency, it was concluded that the oxidation was negative ion-assisted. For an application to insulation layer, the breakdown strength of the oxide film thus produced was also examined, and the value of 6.2 MV/cm was obtained. This value is comparable to that of thermally grown oxide film. The trench oxidation showed a farily high directionality which was dependent on the substrate bias voltage. The value of 1.5 were obtained as the oxidation directionality, defined by the ratio of the oxidation depth of the trench bottom to side wall, while with no bias, the directionarilty was only less than 0.5.

PS-TuP32 Surface Coating of Poly(meta-phenylene isophthalamide) Nanofibers by Chemical Vapor Deposition and Metal Sputtering*, **M. Graham**, W. Liu, D. Reneker, E.A. Evans,* University of Akron

Electrospun nanofibers can be used as either functional or sacrificial substrates for creating nanoscale structures. Surface structures of electrospun nanofibers are of great significance for applications in the areas of filtration, biomedicine, catalyst support and electronics. Coating by chemical vapor deposition (CVD) or physical vapor deposition (PVD) offers a straightforward method to modify the surface properties of nanofibers. Using CVD and/or PVD processes surface roughness, chemical composition, mechanical strength, and electrical conductivity can be controlled. Fibers of poly(meta-phenylene isophthalamide) (MPD-I) were commercialized by the Dupont company under the trademark of NomexÂ®. MPD-I nanofibers were electrospun and collected onto aluminum foil and copper grids as a thin sheet of nonwoven fabric. The average diameter of the as-spun MPD-I fibers was around 200 nm. There was a distribution of fiber sizes. The smallest fiber observed was 4 nm. The fiber surface was relatively smooth. Ultra-thin web-like fibers 3, spring-like fibers and branching fibers were observed, demonstrating the versatility of morphological features produced by electrospinning. Fibers were coated with carbon, copper, aluminum and aluminum nitride using plasma enhanced CVD and PVD processes. TEM, SEM, AFM, and reflectivity measurements were used to characterize the uncoated and coated fibers. MPD-I nanofibers were successfully coated with thin film materials using CVD and PVD processes. The surface features of the fibers were modified so that the roughness, chemical stability, wettability, conductivity and other physical properties of the fiber surface changed or may change accordingly.

Surface Science
Room 134/135 - Session SS+SC-TuP
Semiconductor Deposition Poster Session

SS+SC-TuP1 Fabrication of a-Si:H Films by Plasma CVD*, **T. Nishimiya,*** Mitsubishi Heavy Industries Ltd., Japan

We have succeeded in getting high-deposition rate and high quality for preparing hydrogenated amorphous silicon (a-Si:H) films, as well as micro-crystalline siliconï¼ˆmc-Siï¼‰films, by Very-high-frequency (VHF) plasma CVD using a ladder-shaped electrode. Recently, VHF plasma CVD technique has become one of the topics in the field of the fabrication of solar cell and thin film transistors, because its high plasma density enables high-speed deposition. However, in the large area deposition, which is needed in the application of commercial production, the effective gas flow rate fed into the plasma region limits the deposition rate and the film qualities because the gas depletion condition leads to the degradation of the film quality. We developed the ladder shaped electrode, which has an advantage over a conventional parallel-plate electrode in the controllability of the gas flow. The experiments are performed using a ladder-shaped electrode consisted of 9 stainless-steel rods 160 mmÃ-160 mm in external dimension. The material gases are introduced into the plasma region between each rod of the electrode. Using the VHF-SiH4 plasma at the frequency of 60MHz, we got a-Si:H film at the deposition rate of 1.2 nm/s with the ratio of photo conductivity/dark conductivity of 106. We also applied this electrode to fabricate the mc-Si film and succeed very high-speed of 3.4 nm/s using the plasma of SiH4 diluted with H2 at the frequency of 100 MHz. These were demonstrated that this electrode is highly suitable for the production technique.

SS+SC-TuP2 Growth Characteristics of Si@sub 1-x-y@Ge@subx@C@sub y@ on Si(100) and SiO@sub 2@ in Ultraclean Low-Temperature LPCVD*, Y. Hashiba*, *M. Sakuraba, T. Matsuura, J. Murota,* Tohoku University, Japan

The growth characteristics of Si@sub 1-x-y@Ge@subx@C@sub y@ films on Si(100) and SiO@sub 2@ were investigated. The films were deposited at 550°C in a SiH@sub 4@-GeH@sub 4@-CH@sub 3@SiH@sub 3@-H@sub 2@ gas mixture using ultraclean hot-wall low pressure chemical vapor deposition (LPCVD) system. The total deposition pressure was 30Pa, and the partial pressures of SiH@sub 4@, GeH@sub 4@ and CH@sub 3@SiH@sub 3@ were in the range of 6.0Pa, 0-2.0Pa (Ge fraction x=0-0.57) and 0-0.2Pa (C fraction y=0-0.05), respectively. Si films are epitaxial on Si(100) and amorphous on SiO@sub 2@. The deposition rate of Si on SiO@sub 2@ (1.2-1.4nm/min) is 10-20% larger than that on Si(100), however, with the addition of CH@sub 3@SiH@sub 3@, the deposition rate on SiO@sub 2@ decreases to that on Si(100). It is considered that CH@sub 3@SiH@sub 3@ molecules are scarcely adsorbed at Si-Si pair site on Si(100) but not at the other sites on amorphous Si surface. With the addition of GeH@sub 4@, the deposition rate increases and that on Si(100) becomes larger than that on SiO@sub 2@. Si@sub 1-x@Ge@sub x@ films are epitaxial on Si(100) and or random oriented polycrystalline on SiO@sub 2@. This is explained by the modified Langmuir-type adsorption and reaction with the assumption that SiH@sub 4@ and GeH@sub 4@ are adsorbed more preferentially on the Si-Ge pair site than Si-Si, Ge-Ge pair site, single Si and Ge bond sites. With the addition of CH@sub 3@SiH@sub 3@, the deposition rates decreases and that on Si(100) tends to become the same as that on SiO@sub 2@. It is suggested that the adsorption and reaction of SiH@sub 4@ and GeH@sub 4@ are suppressed by the adsorption of CH@sub 3@SiH@sub 3@ molecule at the Si-Ge pair site. From XPS measurement, Ge fraction on Si(100) is almost equal to that on SiO@sub 2@ within 10% error. The relationship among lattice constant, Ge and C fraction is under investigation.

SS+SC-TuP4 Mechanisms of Vapor Phase Growth of Chalcopyrite Semiconductors*, D.-X. Liao*, *A. Rockett,* University of Illinois

Epitaxial growth of the chalcopyrite-structure semiconductor Cu(In,Ga)Se2 alloys on (111)A and B, (110), and (100) GaAs was studied and a growth model is proposed. These semiconductors are prime candidates for high-efficiency thin film solar cells and have potential in thin film transistor applications. Surface morphologies result from a mixture of surface-energy and nucleation and growth dominated phenomena. Surface energy considerations drive all observed surface planes to decompose into close packed facets, some including large numbers of surface steps. Comparison of the bulk structure and morphologies of the different surfaces indicate that nucleation of surface terraces on close-packed Se-terminated planes and their growth dominates the evolution of surface morphologies. Relatively slow nucleation of terraces on metal terminated close packed planes leaves these very smooth relative to the Se-terminated faces. Structural and electronic properties measurements show that point-defect clusters occur in large numbers in this material and can spontaneously organize on specific planes. The creation of these clusters during facet growth is proposed to be responsible for the observed step motion and consequently for the surface morphologies. Results show that epitaxial temperatures vary significantly from ~700 C on the (111)B surface to ~540 C on (110). The epitaxial temperature is proposed to be related to the availability of Se- and metal-terminated surface step edges. The organization of the point defects during growth appears to lead to a physical separation between the defects responsible for p-type doping and the conduction path for holes, permitting a nearly constant 300K hole mobility of 300 cm2/V-sec over a wide range of hole concentrations.

SS+SC-TuP5 Studies on Spray Deposited Lanthanum Selenide Thin Films from Non-aqueous Medium*, G.D. Bagde*, *C.D. Lokhande,* Shivaji University, India

Since the discovery of high temperature semiconductor, great efforts have been made to produce high quality thin films of the materials. The rare earth chalcogenides are of interest for applications such as thermoelectric cooler, photoelectric cells, solar cells, cold cathode emitting devices, far infrared window materials etc. The rare earth selenide have shown semiconducting properties used for high temperature device formation. Spray pyrolysis is simple and inexpensive technique for large area deposition of thin films. Spray pyrolysis technique is employed to prepare La@sub 2@Se@sub 3@ thin films from non-aquous (methanol) medium. The preparative parameters are optimized to get good quality films. The optimized pyrolysis temperature is 200@super o@C. The La2Se3 film show polycrystalline cubic structure with dominant plane (310). The calculated average grain size is about 40 nm. Scanning Electron Microscopic studies revels that La@sub 2@Se@sub 3@ films have porous fibrous network structure and presence of irregular shaped particles. From the analysis of the optical absorption data a direct allowed transition at 2.45 eV has been observed. The room temperature electrical resistivity is of the order of 10@super 4@-10@super 5@ @ohm@-cm. The films are found to be p-type semiconductor by themoemf measurement study.

SS+SC-TuP6 Studies on Deposition of Indium Sulphide Thin Films by Silar Method*, H.M. Pathan*, *S.D. Sartale, G.D. Bagde, C.D. Lokhande,* Shivaji University, India

Indium Sulphide is a promising material used as a buffer layer in Cu(InGa)Se@sub 2@ based solar cells and mini models. Successive ionic layer adsorption and reaction (SILAR) is a modified version of chemical bath deposition (CBD) method for thin film deposition. In CBD, when solutions are mixed together, the precipitation on the substrate and in the solution takes place. This results into wasteful and unavoidable formation of bulk precipitation in the solution since the reaction is not controllable. To overcome this difficulty, CBD is modified as SILAR in which substrate is immersed into separately placed cationic and anionic precursors and rinsing before every immersion with ion exchanged water to avoid homogeneous precipitation in the solution. In the present investigation, nanocrystalline semiconducting indium sulphide thin films were deposited onto glass substrates using SILAR method. For the deposition of indium sulphide thin films, preparative conditions such as concentration and pH of precursor solution and adsorption, reaction and rinsing time duration were optimized at room temperature (27 @super o@C). These deposited films were characterized for their structural, optical and electrical properties. The films are found to be nanocrystalline. The films have 2.7 eV direct optical band gap with n-type electrical conductivity.

SS+SC-TuP7 The Effects of the Microstructure Factor in Chemical Texturization of Crystalline Si Solar Cells*, F. Krok*, Jagiellonian University, Poland*; Z. Swiatek, E. Beltowska-Lehman,* Polish Academy of Science*; M. Szymonski,* Jagiellonian University, Poland

The texturization of the silicon solar cell front surface improves the cell efficiency due to its antireflection properties and light trapping effect. The chemical texturization of single grains in well-defined multi-crystalline Si wafers was performed in a standard alkaline (anisotropic etching) as well as in acid (isotropic etching) solutions. The microstructure of textured wafers was investigated using SEM, TEM, and NC-AFM methods. The crystallographic orientation of each grain was determined by means of electron back scattered diffraction (EBSD) technique. It comprises the analysis of detected Kikuchi patterns, observed in the SEM. The texturization in alkaline etching solutions causes development of steps between particular grains because of different etching rate in different crystal plane orientation in the wafers. In these cases, although the grains were textured, the grain boundaries became developed and steps were observed. Depending on the grain initial crystallographic orientation (hkl) and the individual disorientation, different final morphologies have been observed. Based on the NC-AFM measurements, the nanostructural nature of the texturized surface was evident for some grain orientations. Moreover, these nanocrystals (ca. 20 nm) have a well-defined preferred crystallographic orientation. The texturized surface with good homogeneity of particular grain orientations of m-c Si has been achieved. The final morphology of the texturized m-cSi surface strongly depends on the process parameters as well as on the polar and azimuthal disorientation of the grain.

SS+SC-TuP8 Polycrystalline Si Thin Film Growth on Glass using Magnetron Sputtering*, **M.J. Jung**, Y.M. Jung, J.U. Kim, J.G. Han,* Sungkyunkwan University, Korea

Polycrystalline Si thin film is widely applied materials for thin film transistor of Flat Panel Display (FPD), and photovoltaic applications because of its high mobility, electrical conductivity, and high-energy conversion efficiency compared to a-Si.@footnote 1@ Over the past few years, there have been a variety of techniques on thin film growth of poly-Si. Among theses techniques, Solid Phase Crystallization (SPC) and Excimer Laser Annealing (ELA) have been the most frequently used methods. The SPC method has too high crystallization temperature (650°C) for glass substrate. On the other hand, ELA method is suitable for low temperature on the glass substrate, however, there are still problems such as non-uniformity of grain growth on the large area glass substrate as well as expensive processing cost.@footnote 2@ Recently, Metal-Induced Crystallization (MIC) of amorphous silicon has been studied for poly-Si thin films on low temperature glass@footnote 3@. We have deposited crystalline poly-Si thin films on soda-lime glass and SiO@sub2@ glass substrate as deposited by PVD at low substrate temperature using high power magnetron sputtering method. The electron mobility of the poly-Si grown on soda-lime glass and SiO@sub2@ glass at substrate temperature of 115° show 138 @cm square per Volt dot second@ and 191@cm square per Volt dot second@. Therefore, to investigate the relationships between surface and film microstructure as well as the nucleation, growth mechanism and its electrical properties of poly-Si thin film, we have studied the variation of plasma state for nucleation and growth mechanism by Langmuir probe and Optical Emission Spectroscopy (OES). The epitaxial orientation, microstructual characteristics and surface properties of the films were analyzed by TEM, XRD, and AFM. For the electrical characterization of these films, its properties were obtained from the Hall effect measurement by the Van der Pauw measurement.

SS+SC-TuP9 Arsenic Incorporation into Indium Phosphide (001) Surfaces during Metalorganic Vapor-Phase Epitaxy*, R.F. Hicks, **D.C. Law**, C.H. Li, S.B. Visbeck, Y. Sun,* University of California, Los Angeles

The quality of heterointerfaces is of great importance for high performance optoelectronic devices. In this work, we report on a detailed study of the effect of arsenic exposure to indium phosphide (001) during metalorganic vapor-phase epitaxy (MOVPE). Indium phosphide surfaces were exposed to several Torr of tertiarybutylarsine (TBAs) at temperatures ranging from 200 to 600°C. Scanning tunneling micrographs reveal that arsenic exposure below 400°C yields atomically smooth surfaces with ordered reconstructions. These surfaces consist of either a single monolayer of As and P with a (2x1) structure, or half a monolayer of As incorporated into a (2x4) structure. Conversely, at temperatures above 450°C, three-dimensional islands are formed during TBAs exposure. The arsenic coverage in these structures exceeds several monolayers, indicating diffusion into the bulk. The implications of these results for the fabrication of III- V heterojunction devices will be discussed at the meeting.

SS+SC-TuP10 Synthesis of Sb2Se3 Nanorods under Mild Hydrothermal Conditions*, J. Wang, **Z. Deng**, Y. Li,* Tsinghua University, P.R. China

A hydrothermal reduction route was employed for the synthesis of Sb2Se3 semiconductor nanorods. The reaction temperature for the formation of Sb2Se3 nanorods was found to be above 130Â°C, otherwise some impurities, such as Sb2O3 and unreacted Se, would exist in the final products. In addition, the role of hydrazine, which serves as both the reducing agent and the coordinator, was also found to be crucial for the formation of the rod-like products. The resulted products were characterized by XRD, TEM, XPS, UV-vis adsorption spectroscopy and Raman spectroscopy. @FootnoteText@ Email: ydli@@tsinghua.edu.cn Tel.: +86-10-62772350 Fax: +86-10-62788765 .

Surface Science

Room 134/135 - Session SS1-TuP

Semiconductor Surfaces Poster Session

SS1-TuP3 Reduction of Oxidation Rate during the Initial Stages of the Oxidation of Heavily Phosphorus Doped Silicon in Dry Oxygen*, **Y. Kamiura**, K. Hasegawa, Y. Mizokawa,* Osaka Prefecture University, Japan*; K. Kawamoto,* Denso Co. Ltd., Japan

The oxidation of heavily phosphorus doped Si(100) and polycrystalline Si in RT to 800°C range in dry oxygen was studied by Auger electron spectroscopy(AES). The oxidation rate of the phosphorus doped Si(100) was larger than the P-doped poly-Si for each O@sub 2@ exposure at RT. Phosphorus segregation didn't take place in RT oxidation of the P-doped Si(100). The Dioxide formation gradually occurred from ca. 500L in thermal oxidation at 650°C in the P-doped Si(100). The reduction of oxidation was found above 5x10@super 5@L. At the same time, the amount of the phosphorus piled-up at Si/SiO@sub 2@ interface slightly degreased. The accurate AES measurements of 97 to 137eV range showed that phosphorus slightly oxidized in the initial stage of the oxidation of P-doped Si for each O@sub 2@ exposure and the phosphorus peak in P@sub 2@O@sub 5@ was clearly found at ca. 110eV above 10@super 3@L. It seemed that the modification of this substance fairly desorbed in UHV and the residual partially held into the Si/SiO@sub 2@ interface at this temperature. Therefore the oxidation of silicon didn't proceed until about ca. 1x10@super 6@L. On the other hand, the suppression of oxidation of silicon wasn't caused for P-doped poly-Si, the amount of SiO@sub 2@ strongly increased above 5x10@super 5@L. The thermal oxidation behavior at 800 °C was quite different from low temperature results. Oxygen uptake on the silicon surfaces didn't almost take place below 10@super 3@L for both samples because the volatile SiO molecules were formed and the silicon surfaces were etched away by oxygen atoms. Dioxide formations rapidly took place above 10@super 4@L, and then a large amount of phosphorus piled up at the interfaces due to the formation of SiO@sub 2@. The P@sub 2@O@sub 5@ was formed through low O@sub 2@ exposures even at this temperature for both samples.

SS1-TuP5 The Investigation of the Semiconductors Surfaces by Method of the Low Energy Ion Scattering*, **U. Kutliev**, B. Kalandarov,* Urgench State University, Uzbekistan

In the present work the scattering processes of 5 keV Ne @super +@ ions on the GaP(100) surface under grazing ion bombardment have been investigated by computer simulation in the binary collision approximation. The particle interaction were described by the universal BZL-potential. Elastic and inelastic energy losses of scattered ions were summed along their trajectories. Trajectories of incident ions experienced correlated sliding scattering on discrete atomic chains, in semichannels and channels in the , <-100> directions were traced in several nearest to surface atomic layers. The monoatomic steps of the different length, one atomic layer high on the surface were simulated. Energy, angular and spatial distributions of Ne @super +@ ions scattered from stepped GaP(100) surface at different crystal directions were calculated. The computer simulation allowed an investigation of the effect of the atomic steps on the real single crystal surface upon the trajectory features and capture in subsurface channeling and dechallening of the ions being scattered on the surface. It has been shown that the presence of atomic steps on the surface lead to increase of the capture probability of channeling ions in the layers under the steps and to increase of probability of their dechanneling. Character of ions movement under the step (their range, energy losses and dechanneling) is determined both the grazing angle and capture angle under the step.

SS1-TuP6 Femtosecond Time-Resolved Photoemission Study of Two-Dimensional Layered Semiconductor MoS@sub 2@ Surface*, **A. Tanaka**,* Tohoku University, Japan and University of Rochester, JAPAN*; N.J. Watkins, Y. Gao,* University of Rochester

A femtosecond time-resolved two-photon photoemission study of 2H-MoS@sub 2@ surface has been carried out in order to investigate in detail the relaxation dynamics of hot electrons in the two-dimensional layered semiconductor. Among the lamellar transition metal dichalcogenides, MoS@sub 2@ is a semiconductor with an indirect gap of about 1.2 eV. The observed two-photon photoemission spectrum with a photon energy of 3.3 eV exhibits a single feature in the intermediate state energy between 2.1 and 3.3 eV above the valence-band maximum (i.e., between 0.9 and 2.1 eV above the conduction-band minimum). From the detailed time-resolved two-photon photoemission measurements as a function of electron excitation energy, it is found that the inverse relaxation lifetime of hot electrons depends linearly on the excess energy above the conduction-band minimum. This result is in strong contrast to the results based on the Fermi liquid theory, which takes into account the electron-electron scattering as the dominant relaxation process and gives the quadratic energy dependent lifetime in the both three- and two-dimensional electron systems within logarithmic corrections. From these results, we discuss the relaxation process of hot electrons in the two-dimensional layered semiconductor.

Surface Science
Room 134/135 - Session SS2-TuP
Semiconductor Reactions Poster Session

SS2-TuP1 XPS Investigation of Trimethylsilane Dosed Ge (100) Surfaces*, **P.W. Wang**,* The University of Texas at El Paso*; Y. Qi,* University of Massachusetts*; J.H. Craig,* Bradley University

Trimethylsilane (TMSi) was dosed onto a sputter cleaned Ge (100) surface at 145 + 5 oC and X-ray photonelectron spectroscopy (XPS) was used to study the cumulative effect of dosage, electron irradiation, temperature, and X-ray photon irradiation. The core level C 1s, Si 2p and Ge 3d photoelectrons were monitored. Arguments based on electronegativities of C, Si, and Ge and bond strengths of C-C, C-Si and C-Ge are invoked to interpret the interaction of TMSi with the Ge (100) surface under various external conditions. It is demonstrated that TMSi dissociatively chemisorbs initially at low coverage, but physisorbs molecularly at high coverage. Both electron irradiation and thermal effects cause the breaking of C-C or C-H bonds. New bonds of C-Ge are formed as a consequence. X-ray photon induced secondary electrons and local heating result in the dissociation of the adsorbed C-H or Si-H species which causes the initial concentration increase of Ge-C bonds. This study clearly shows the different pathways to form new species on the Ge (100) surfaces under various external conditions.

SS2-TuP3 Generation of Type-C Defects on Si(100) by Bimolecular Adsorption of Water: A FT-IR, STM, AES and QMS Study*, **M. Nishizawa**, T. Yasuda, S. Yamasaki,* Joint Research Center for Atom Technology (JRCAT), Japan*; K. Miki,* National Institute of Advanced Industrial Science and Technology (AIST), Japan*; M. Shinohara, N. Kamakura, Y. Kimura, M. Niwano,* Tohoku University, Japan

STM studies on various processes on Si(100)-(2x1) are often interfered with a high density of surface defects. Among three types of defects reported on this surface,@footnote 1@ the structure of the so-called type-C defect has been under debate. We show that the C-defects are generated by adsorption of water from the UHV environment. This conclusion is based on our systematic investigations using FT-IR, STM, AES, and QMS. Our STM experiments have reproduced the commonly observed phenomenon that the C-defect density increases with time even when the vacuum is as good as 10@super -11@ Torr. The surface with many C-defects shows a small but detectable O@sub KLL@ signal in AES. A possible source of O is the residual H@sub 2@O, CO, and/or CO@sub 2@ in UHV. To identify the source of surface O, we examined the correlation between the generation rate of the C-defects and the partial pressures for these gases. We have found that H@sub 2@O, which adsorbs at a sticking probability near unity, is the only candidate that can account for the defect generation rate. Dissociative adsorption of residual H@sub 2@O has been indeed detected by our IR measurements in which Si-H and O-H stretching modes are observed. The Si-H band has two components indicating that there are two kinds of Si-H bonds of different configurations. In addition, kinetic analyses of the Si-H evolution have revealed that the adsorption takes place via highly mobile precursor states. These observations suggest that C-defects are generated by bimolecular adsorption of H@sub 2@O, which readily explains the STM observation that the C-defects occupy two dimers. The detailed structure of the C-defect will be discussed at the presentation. This study, partly supported by NEDO, was performed at JRCAT under the joint research agreement between AIST and ATP. @FootnoteText@ @footnote 1@ Hamers et al., J. Vac. Sci. Technol. A 7 (1989) 2854.

SS2-TuP5 Investigation of Surface Intermediates in Thermal Decomposition of Diethylmethylsilane on Si(111) using Low Energy Cs Ion Scattering and Thermal Desorption Spectroscopy*, **H.-G. Chi**, Y. Kim, J.-H. Boo, S.K. Kim, S.-B. Lee,* Sungkyunkwan University, Korea*; H.T. Kwak,* Kook Min University, Korea

The intermediate species produced in the decomposition of diethylmethylsilane on Si(111) were investigated in the range of 110 1200 K by using Cs@super +@ reactive ion scattering (RIS), low energy secondary ion mass spectrometry (SIMS) and thermal desorption spectroscopy. We will show that RIS gives more reliable evidence than SIMS for identification of surface species of this system. The results of low energy Cs@super +@ ion scattering indicate that molecular diethylmethylsilane and various alkylsilyl species such as (C@sub 2@H@sub 5@)@sub 2@Si, C@sub 2@H@sub 5@SiCH@sub 3@, C@sub 2@H@sub 5@Si, and CH@sub 4@Si as well as hydrocarbon species such as C@sub 2@H@sub 4@ and C@sub 2@H@sub 5@ exist on surface between 110-150 K. Above 300 K, all the alkylsilyl species are converted to CH@sub 4@Si, which decomposes completely to form SiC above 900 K. We will propose a possible mechanism for the SiC formation from the results of low energy ion scattering and thermal desorption spectroscopy.

SS2-TuP6 Interface Reaction of Cesium Layers Deposited on a H-terminated CVD Diamond*, **S. Yoshida**, T. Inaba, T. Urano, S. Hongo,* Kobe University, Japan

CVD diamond is potential for negative electron affinity (NEA)materials. Therefore, H-terminated and alkali adsorbed diamond surfaces have been studied intensively. It has been known that getting clean diamond surface is difficult. Because Ar ion sputtering and electron irradiation may result in amorphization of the diamond structure and heating the amorphous layer results in the formation of graphitic clusters. Cyclic adsorption and desorption of hydrogen also degrades the surface. Like this, the diamond surface is complicated and has inherent instability compared with Si surface. Therefore it is neccessary to reveal interface reaction to produce stable NEA devices. In this study hot-filament CVD diamond was used. All experiments were carried out in a UHV chamber equipped with thermal desorption spectroscopy, metastable deexcitaion spectroscopy, ultra violet photoelectron spectroscopy and Auger electron spectroscopy (AES). Cesium was deposited using SAES gettters Cs dispenser at 150 K. Atomic hydrogen produced by hot filament was used to terminate the diamond surface. It was found that 1)Multilayer(island) Cs is formed on Ar ion sputtered surface, 2)Multilayer(island) Cs desorption peak is not observed on a H-terminated surface, 3)Clear H@sub2@ desorption peak attributed to Cs-H bond foirmation (which is seen for Cs/H-terminated Si(100) sample) is not observed for Cs/H-terminated CVD diamond, 4)As raising the sample(Cs/H-terminated CVD diamond) temperature from 150 K to 470 K, AES peak of Cs decreases and that of C increases, though no Cs and H@sub2@ desorption peak are observed during heating. These experiments may suggest the formation of Cs-C-H mixture at low temperatures.

Surface Science
Room 134/135 - Session SS3-TuP
Adsorption/Desorption Poster Session

SS3-TuP3 The Evolution of Surface Topography of Alkali Halides Crystals During Ion Stimulated Desorption*, F. Krok, J.J. Kolodziej, B. Such, P. Czuba, P. Piatkowski, **M. Szymonski**,* Jagiellonian University, Poland

Ion-stimulated-desorption (ISD) of alkali halide (RbI, KBr) surfaces under 5 keV He+ bombardment is investigated in UHV by means of non-contact Atomic Force Microscopy (nc-AFM) and Quadrupole Mass Spectroscopy (QMS). Irradiated surface topography and corresponding desorption fluxes are studied. Although, for the energy range of He+ ions used in the present work, desorption of alkali halides occurs predominantly via electronic processes, there are significant differences between ISD and the electron stimulated desorption (ESD). Recently, present authors@footnote 1,2@ have demonstrated that ESD of alkali halides proceeds in a layer-by-layer mode and oscillating desorption fluxes are observed. These ESD oscillations have been explained to be due to creation of Frenkel pairs in the bulk, their diffusion, and their recombination with surface modulated accordingly to changing surface topography. For ISD studied in the present work AFM images show that the surface erosion does not follow the layer-by-layer scheme and no oscillation in desorption fluxes are found. We propose that these (not anticipated) differences between electron- and ion- stimulated desorption are caused by ballistic processes at the surface. While most of the primary ion beam energy is deposit deep in the bulk leading to production of Frenkel pairs some projectiles colliding violently with top-layer ions may introduce additional nucleation centers for vacancies on surface. Moreover the shallow collision cascades, which extend to the top crystal layers are likely to induce mobility in alkali halide top crystal layer. These ballistic processes interfere with electronic processes and destroy the layer-by-layer desorption scheme. @FootnoteText@@footnote 1@B. Such, J. Kolodziej, P. Czuba, P. Piatkowski, P. Struski, F. Krok and M. Szymonski, Phys. Rev. Lett., 85 (2000) 2621. @footnote 2@R. Bennewitz, S. Schar, V. Barwich, O. Pfeiffer, E. Meyer, F. Krok, B. Such, J. Kolodziej, M. Szymonski, Surf. Sci. Lett., 474 (2001) L197.

SS3-TuP4 Nano-scale Modification of Ionic Surfaces by ESD*, **B. Such**, J.J. Kolodziej, P. Czuba, P. Piatkowski, P. Struski, F. Krok, M. Szymonski,* Jagiellonian University, Poland

Surface modification of alkali halide crystals by electron beam was investigated with the use of dynamic force microscope (DFM). It was found that randomly spread rectangular pits of monolayer depth, in the topmost layer of the crystals, were formed during irradiation. Growth and coalescence of the pits led to almost layer-by-layer desorption mode. Average size and density of the pits could be changed by varying parameters of an electron beam and surface temperature leading to controlled nano-modification of the surface. Moreover, by comparison of DFM and mass spectroscopy data we were able to establish that the surface stepdensity, changing in time, controlled the desorption process. The new model of electron-stimulated desorption (ESD) of alkali halides was proposed to explain observed behavior, based on the idea of existence of two kinds of F-centers in the crystal: ground state (immobile) and excited (mobile) ones.

SS3-TuP5 The Simultaneous Observation of Adsorption Isobars of Xe/Ag(111) and Xe/Ag(100)*, A. Tosaka*, *T. Mitake, T. Hirayama, I. Arakawa,* Gakushuin University, Japan

The growth and the structure of a Xe film physisorbed on the surface of a silver single crystal, Ag(111) or Ag(100), have been investigated by means of an ellipsometry and an eXtremely-low-current LEED (XLEED). We obtained adsorption isobars of Xe/Ag(111) and Xe/Ag(100) simultaneously: one was observed by the ellipsometry and the other by the spot intensity measurement of XLEED in the temperature range between 60K and 90K and the equilibrium Xe pressure range between 5X10@super -6@Pa and 2X10@super -4@Pa. The first layer condensation of Xe/Ag(111) occurs at the temperature 0.3±0.1 K higher than that observed for Xe/Ag(100), while the second layer condensation occurs at the same temperature within the experimental accuracy . On the assumption (1) that this temperature difference is mainly caused by the difference of the induced dipole moment between the Xe atom on Ag(111) and that on Ag(100) and (2) that the system follows the two dimensional van der Waals equation, we calculated the difference of the induced dipole moment μ to reproduce the experimentally determined temperature difference. The result shows that μ on Ag(100) is 5% larger than that on Ag(111). @FootnoteText@ *T. Hirayama Present Address: Department of Physics, Rikkyo University, Toshima, 171-8501 JAPAN.

SS3-TuP6 Measurement and Quantitative Analysis of Photon or Electron Stimulated Desorption Yields of Solid Argon and Krypton*, T. Adachi*, *T. Hirayama,* Gakushuin University, Japan*; M. Sakurai,* Kobe University, Japan*; I. Arakawa,* Gakushuin University, Japan

Electron or photon irradiation of the surface of rare gas solids produces the electronic excitations which can be followed by the desorption of various kinds of particles. Investigation of the desorption characteristics such as desorption yields, kinetic energy distributions and angular distributions, will reveal the dynamics of the electronic excitations and relaxations in rare gas solids. We have reported the absolute photo-desorption yields of solid neon at the excitonic excitation energy range and shown that the yields were quantitatively explained by an internal sputtering mechanism.@footnote 1@ Here, we present the absolute desorption yields of the solid argon and krypton for the both case of photon impact and low energy electron impact. At the films thicker than 400 atomic layers, the absolute photo-desorption yields were about 1.5, 0.07, and 0.03 atoms/photon for neon, argon, and krypton, respectively, at the excitation energy of first order bulk exciton. In the case of 220 eV electron impact, the desorption yields were about 1 and 0.1 atoms/electron for argon and krypton, respectively. We will present the quantitative evaluation of the absolute desorption yields and these thickness dependencies for argon and krypton using the the classical molecular dynamics calculation results.@footnote 2,3@ @FootnoteText@ *T. Hirayama Present address: Department of Physics, Rikkyo University, Toshima, Tokyo 171-8501 JAPAN. @footnote 1@ Arakawa, I., et al. Surf. Sci. 451, 136 (2000). @footnote 2@ Cui, S., et al. Surf. Sci. 207, 186 (1988). @footnote 3@ Dutkiewicz, L., et al. Nucl. Instr. Meth. B 101, 188 (1995).

SS3-TuP7 The Adsorption and Thermal Decomposition of Trimethylamine on Si(100)*, L.H. Zhang*, *A.J. Carman, J. Liswood, S.M. Casey,* University of Nevada, Reno

Trimethylamine (TMA) adsorption on Si(100)-(2x1) has been investigated using low-energy electron diffraction, Auger electron spectroscopy (AES), and thermal desorption spectroscopy (TDS). TMA appears to undergo molecular adsorption on this surface at room temperature. By comparison to the AES results from the adsorption of methyl iodide on Si(100), it was concluded that the initial surface saturation coverage of TMA on Si(100) is 0.5 monolayers. TDS reveals a parent TMA desorption channel, as well as competing surface decomposition channels. In order to gain further physical insight into the available reaction pathways for this molecule on this surface, we have used density functional theory (DFT) to study the adsorption of TMA on simplified silicon clusters. By experimental and theoretical studies of the adsorption of TMA and its subsequent surface pyrolysis, we try to understand the bonding characteristics and possible deposition reaction pathways for TMA and similar amines on the surfaces of semiconductor wafers.

SS3-TuP8 Resonances in Electron-Stimulated Desorption of Europium Atoms from Oxidized Tungsten: Effects of Temperature*, V.N. Ageev*, Academy of Sciences of Russia, Russia*; Yu.A. Kuznetsov, N.D. Potekhina,* Academy of Sciences of Russia*; T.E. Madey,* Rutgers, The State University of New Jersey

The electron-stimulated desorption (ESD) yield for neutral europium (Eu) atoms from Eu layers adsorbed on oxidized tungsten surfaces has been measured as a function of electron energy, europium coverage and degree of oxidation of tungsten, with an emphasis on effects of substrate temperature. The measurements have been carried out using a time-of-flight method and surface ionization detector. We expand on an earlier report, and compare ESD of multivalent Eu with ESD of monovalent alkali atoms, studied previously. The Eu atom ESD is a complicated function of Eu coverage, electron energy and substrate temperature. In the coverage range 0.05 to 0.35 monolayer (ML), overlapping resonant-like Eu atom yield peaks are observed at electron energies of 36 and 41 eV that might be associated with Eu 5p and 5s level excitations. Additional resonant - like peaks are seen at electron energies of 54 and 84 eV that are associated with W 5p and 5s level excitations. The Eu atom yield peaks at 36 and 41 eV are seen only in the temperature range 220 to 300 K at an europium coverage of 0.07 ML, and the temperature range becomes narrower with increasing europium coverage. In contrast, the peaks at 54 and 84 eV persist above 500 K. The surface ionization current calculations show that the yield associated with the tungsten core level excitations may arise from the ESD of EuO molecules rather than Eu atoms. This is the only reported system for which the electron energy dependence of neutral ESD yield has a resonant character, in the absence of a non-resonant background.

SS3-TuP9 Cs Adsorbed Structure and Change of Magnetism in fcc Co Thin Films Grown on Cu(001) Surfaces*, F. Komori*, *M. Xu, T. Iimori, K. Lee, M. Yamada, K. Nakatsuji,* ISSP, University of Tokyo, Japan

Magnetic properties of ferromagnetic thin films are often largely modified by adding foreign atoms on the surface. Some of the adsorbed non magnetic atoms or molecules make the magnetization small and change the magnetic anisotropy. To study the effect of Cs adsorption on magnetism as a simple metal, we have deposited Cs on a fcc Co(001) thin film grown on a clean Cu(001) surface, and measured correlation between the ordered structure of Cs adsorbed surface and the ferromagnetic hysteresis loops of the thin film. A fcc Co thin film (about 5 mono-atomic layers thick) was prepared on a clean Cu(001) surface in an ultra-high vacuum, and the surface structure was monitored by LEED with increasing the amount of adsorbed Cs both at 300 K and at 100 K. In both cases, a ring pattern appeared at the first stage of the deposition, and then quasihexagonal LEED spots with two domains were observed. These features are similar to the Cs adsorption on a clean Cu(001) surface, and the distance between the adjacent Cs atoms on the Co surface is the same as that on the clean Cu surface. The relation between the ferromagnetic hysteresis loops and the amount of the adsorbed Cs was in situ studied using magneto-optical Kerr effect. Cs adsorption does not change the magnitude of the magnetization. This is quite in contrast with hydrogen adsorption on the same surface. With increasing the amount of Cs on the surface, the coercive force once decreases and then increases at 100 K while it is almost constant after the initial decrease at 300 K. These are interpreted the increase of the uni-axis magnetic anisotropy due to the steps on the surface at 100 K..

SS3-TuP10 Real-Time Monitoring of Desorption and Restoration on Cl/Si(111) Surface with Second Harmonic Generation*, K. Shudo*, *T. Sasaki, M. Tanaka,* Yokohama National University, Japan

Surface etching with halogen is most elementary process in semiconductor fabrication. To elucidate thermal process on Cl-covered Si(111)-1x1 surface, second harmonic (SH) generation was measured in real time with 1.17 eV photons from a pulsed laser (8 nsec). From isothermal change in the SH signal, energetics on related reactions can be discussed. On clean Si(111)-7x7 dimer-adatom-stackingfault (DAS) surfaces, SH intensity was calibrated in Cl-adsorption compared with temperature programmed desorption. The weakened SH signal by disappearing dangling bonds was interpreted as chlorine coverage on the surface. Initial sticking probability of Cl on the surface was determined to be 0.58, that is actually the same as obtained with SDR.@footnote 1@ Under the isothermal treatment of the Cl/Si(111)-1x1 surface from 843 to 963 K, time-evolution of SH recovery showed that fast and slow steps are involved in the process. The fast one turned out to be of a first order process. Temperature dependence of the rate in the fast component indicates a barrier of 2.1 eV. It corresponds to an energy against emerging of dangling bonds at desorption of silicon chlorides. The following slow component has 2.4 eV of barrier, being activation energy to reform the surface into 7x7 DAS structure. To reduce the dangling bond, 5x5 or 9x9 structures are known to appear temporarily before 7x7 DAS appears. The barrier is considered as the energy required for the slow structural restoration to form and/or move stacking faults. @FootnoteText@ @footnote 1@ Desorption from Cl/Si(111) is also discussed with surface differential reflectance (SDR) spectroscopy, presented elsewhere of SS17 in the conference.

SS3-TuP11 Adsorption and Decomposition of Dimethylisopropylsilane on Si(111) Surface*, **T.S. Yang**, S.J. Cho, J.-H. Boo, J.-W. Lee, S.-B. Lee,* Sungkyunkwan University, Korea*; Y. Kim,* Korea Research Institute of Chemical Technology, South Korea

The adsorption and decomposition of dimethylisopropylsilane,(CH@sub 3@)@sub 2@CHSiH(CH@sub 3@)@sub 2@ on Si(111) surface have been studied in the temperature range of 100 - 1200 K in ultrahigh vacuum by X-ray photoelectron spectroscopy, thermal desorption spectroscopy, and low-energy Cs ion reactive scattering. Dimethylisopropylsilane adsorbs molecularly on the surface at 115 K and its thermal desorption spectrum shows a board peak centered at about 250 K. Even at this low temperature, the results of the low-energy Cs ion reactive scattering indicate that the adsorbed dimethylisopropylsilane was found to partially decompose to adsorb as the Si(CH@sub 3@)@sub 2@ and (CH@sub 3@)@sub 2@CHSiH species. The former decomposes to form CH@sub 4@Si and C@sub 2@SiH@sub x@ species with increasing temperature up to about 600 K and the latter may be converted C@sub 3@H@sub y@ on the surface. Above 900 K the intermediate species completely decomposes to form SiC. The possible decomposition mechanism of dimethylisopropylsilane will be proposed.

SS3-TuP12 Negative Ion Formation in Electron-Stimulated Desorption of CF@sub2@Cl@sub2@ Co-adsorbed with Polar and Non-polar Gases on Ru(0001)*, **S.M Solovev**,* A. F. Ioffe Physico-Technical Inst., Russia*; D. Kusmierek, T.E. Madey,* Rutgers University

Photon-induced dissociation of CF@sub2@Cl@sub2@ (freon-12) in the stratosphere contributes substantially to atmospheric ozone depletion. We report recent results on dissociation and negative ion formation in electron-stimulated desorption of CF@sub2@Cl@sub2@ on Ru(0001), when CF@sub2@Cl@sub2@ is coadsorbed with a polar gas (NH@sub3@) and non polar Xe, for electron energies from 50 eV to 300 eV. Two different time-of-flight methods were used in this investigation : (a) an ESD ion angular distribution (ESDIAD) detector with wide collection angle, and (b) a quadrupole mass spectrometer with narrow collection angle and high mass resolution. Many negative ESD fragments are seen (F@super-@, Cl@super-@, FCl@super-@, CF@super-@, F@sub2@@super-@, Cl@sub2@@super-@, CFCl@sub2@@super-@, whose intensities depend on the surface preparation. Using both detectors we observe a giant enhancement of Cl@super-@ and F@super-@ yields for ESD of CF@sub2@Cl@sub2@ coadsorbed with ~1ML of NH@sub3@; this enhancement (> 10@super3@ for Cl@super-@) is specific to certain ions, and is attributed to an increased probability of dissociative electron attachment due to "trapped" low-energy secondary electrons.@footnote 1@ The magnitude of Cl@super-@ yield enhancement as a function of electron energy scales with the secondary electron yield, demonstrating the role of low-energy secondaries. In further studies, the influence of polar NH@sub3@ and non-polar Xe space layers (1-10 ML) on ESD of top-layer CF@sub2@Cl@sub2@ is determined, and compared with thick films of condensed CF@sub2@Cl@sub2@. The magnitudes and energy-dependences of the Cl@super-@ yields are different in these cases, due to several contributing factors. @FootnoteText@ @footnote 1@ Q. - B. Lu and T. E. Madey, Surf. Sci. 451(2000) 238.

SS3-TuP13 Collision Induced Process of Adsorbates on Ni(100)*, T. Takaoka, M. Inamura, S. Yanagimachi, **I. Kusunoki**,* IMRAM, Tohoku University, Japan

Surface reactions are usually described as reactions between adsorbates on surfaces. However, effect of collision of molecules in gas phase to surfaces is drawing attention at present. In this work, the collision effect on a N@sub 2@ monolayer, a benzene multilayer, and CO and H coadsorbates on Ni(100) surfaces were investigated. The experiment was carried out in the homemade molecular beam apparatus, which was equipped with a FTIR spectrometer. A supersonic molecular beam technique was used for the control of translational energy of Xe atoms. (1) N@sub 2@ on the Ni(100) surface In FTIR spectra of a Ni(100) c(2x2)-N2 surface, a peak was observed at 2205 cm@super -1@. From the analysis of FTIR spectra recorded after the surface began to be irradiated with Xe beam, it was found that the desorption of N2 molecules is induced by collision with the Xe atoms. The desorption is induced when Xe energy is above threshold energy of 0.8 eV. The threshold energy can be explained with a classical collisional model. (2) benzene multulayer on the Ni(100) surface The effect of the collision onto a multilayer of molecules has been studied. No desorption was observed when a benzene multilayer on the Ni(100) surface was irradiated with Xe atoms with energy of 1.2 eV. The energy transferred from the Xe atom was probably dissipated in condensed molecules and no desorption was observed. (3) CO and H coadsorbates on the Ni(100) surface After the Ni(100) surface was pre-exposed to H@sub 2@ and subsequently exposed to CO, a peak at 2100 cm@super -1@ was observed. In FTIR spectra recorded after the surface began to be irradiated with the Xe beam, decrease of the intensity of the 2100 cm@super -1@ peak and increase of the intensity of a 1950 cm@super -1@ peak with increasing Xe irradiation were observed. It was found that the adsorption site of CO is changed owing to the collision of Xe atoms and a cross section for the change is dependent on the Xe energy.

SS3-TuP14 Desorption of Silicon Chloride and Formation of Dimer-Adatom-Stacking Fault Structure on Si(111) Studied by Surface Differential Reflectivity Spectroscopy*, **M. Tanaka**, S. Minami, K. Shudo,* Yokohama National University, Japan

The processes of isothermal desorption of silicon chloride from the chlorine-saturated Si(111)1x1 surface has been investigated by means of in-situ real-time surface differential reflectivity (SDR) spectroscopy. Temperature range was 873-933K. SDR spectra at each temperature were obtained by the normalization with the reflectance spectrum of the clean surface having 7x7 dimer-adatom-stacking fault (DAS) structure. The spectral features observed at 1.8 and 2.5eV come from missing of adatom dangling bonds and adatom back bonds of DAS structure, respectively. The feature at 1.8eV is found to be removed faster than that at 2.5eV due to the desorption of silicon chloride, which means that the feature at 1.8eV originates from not only adatom dangling bonds but also dangling bonds on the 1x1 surface. The restoration of the dangling bonds therefore represents the development of the desorption. The desorption process is found to follow first order kinetics, suggesting the mechanism that SiCl supplied from clusters and/or steps on the chlorine-saturated Si(111)1x1 surface recombines with Cl on the surface and SiCl@sub 2@ species is desorbed. The activation energy of this process is obtained as 2.2eV from the temperature dependence of the rate constant. On the other hand, the restoration of the back bonds represents the formation of DAS structure after the desorption. The restoration process is found to follow also first order kinetics, and the activation energy is obtained as 2.8eV. The mechanism of the desorption of silicon chloride and the formation of DAS structure is discussed from these activation energies in terms of potential barriers.

SS3-TuP15 Spatially Resolved Thermodynamic and Kinetics of Adsorption on BaTiO@sub 3@ Surface by Variable Temperature Scanning Probe Microscopy*, S.V. Kalinin, D.A. Bonnell, **S. Gupta**,* University of Pennsylvania

Variable temperature scanning surface potential microscopy is used to determine thermodynamic and kinetic parameters associated with polarization and charge dynamics on BaTiO@sub 3@ (100) surface. Potential retention above the ferroelectric phase transition, observation of domain wall motion, and local piezoresponse indicate that the temperature dependence of surface potential results from the interplay between the fast dynamics of atomic polarization and slower dynamics of screening charge. At room temperature surface potential has the sign of the screening charges and is reverse to that expected from polarization orientation. Increasing the temperature results in a decrease of polarization charge leaving the screening charges uncompensated, thus increasing the effective surface potential. On decreasing the temperature spontaneous polarization increases and for a short period of time sign of domain potential is determined by the polarization charge. This phenomenon is referred to as temperature induced potential inversion (TIPI). Under isothermal conditions, polarization and screening charges equilibrate and the potential returns to an equilibrium value. The relaxation kinetics are found to be weakly dependent on temperature with activation energy E@sub a@ ~ 4 kJ/mole. The equilibrium domain potential difference was found to be linearly dependent on temperature. A thermodynamic description of ferroelectric screening based on the Ginzburg-Devonshire theory was developed and enthalpy and entropy were obtained as @Delta@H@sub ads@ = 164.6 kJ/mole, @Delta@S@sub ads@ = -126.6 J/mole K for BaTiO@sub 3@ (100) surface in air. These values are within the range expected for adsorption from the gas phase. Thus, in the case where the charge compensation mechanism is surface adsorption, scanning probe microscopy allows kinetics and thermodynamics of adsorption to be studied with the advantage of spatial localization over techniques such as temperature programmed desorbtion.

SS3-TuP16 COsmic COcktails: CO-ice Chemistry under Interstellar Conditions*, **H.J. Fraser**, W.A. Schutte, E.F. van Dishoeck,* Leiden University, Netherlands

Ices are observed throughout the universe: on planetary bodies, comets, in the Interstellar Medium and in protoplanetary disks. In the laboratory it is possible to study the chemistry and physics of molecular ices under pseudo interstellar conditions. Our experiment combines UHV surface science techniques with an atomic beam to study chemical reactions occurring on interstellar ice grain mimics. The experiment is aimed at identifying the key barrierless reactions and desorption pathways on ices of H@sub 2@O and CO that generate simple molecular species in the gas phase. In this poster we will present results illustrating the desorption rate of CO ice when H@sub 2@ is formed from H recombination reactions on the ice surface, and identify the reaction products formed during thermal warm-up, e.g. HCO, CO@sub 2@, H@sub 2@O, HCOOH. We will also present results on the reaction between CO and O, before, during and after ice processing by UV irradiation. The chemical and astronomical implications of these results will be discussed.

SS3-TuP17 Phosphorus Behaviors upon the Annealing of the Heavily Phosphorus Doped Silicon with Thin Native Oxide Film Evaluated by XPS and AFM*, **Y. Mizokawa**, W.B. Ying, H. Iguchi, Y. Kamiura,* Osaka Prefecture University, Japan*; K. Kawamoto,* Denso Co. Ltd., Japan

Phosphorus redistribution and its chemical structure of the heavily phosphorus doped Si(100) upon the annealing were investigated using x-ray photoelectron spectroscopy (XPS) and atomic force microscope (AFM). The samples were prepared by predeposition of POCl@sub 3@, and annealing was performed on the HF-treated samples with about 2nm-thick native oxide film in nitrogen atmosphere at 450°C, 660°C and 750°C for 1 hour. The depth profiling was carried out by the chemical etching using 0.1-1% HF solutions. The true in-depth profiles of P obtained after correcting the mean free path effect showed that the segregated-P was piled up at the interface, and its concentration decayed exponentially toward both directions of oxide film and substrate. Although the dominant chemical structure of P was unoxidized states throughout the oxide/Si, the peak position of the P2p photoelectron shifted toward higher binding energy side with approaching the interface. The results suggest that upon annealing a part of the segregated P atoms located in the top surface region of silicon lattice protrude into the oxide film as a form of P-cluster with P-P bonding. The amount of protruded-P in the oxide film increased with annealing temperature, where the activation energy was about 1 eV. The amount was estimated to be about 1x10@super 15@ P-atoms/cm@super 2@ after 750°C annealing. The AFM image showed an unique pattern of various-sized plateaus of about 2nm height, and after 750°C annealing, some of the plateaus grew in height keeping their lateral shape. The total increments were in rough accord with the estimated volume of protruded-P in the oxide film.

SS3-TuP18 Vibrational Excitation of Methane Physisorbed on Ag(111) using HREELS*, **M. Sakurai**, S. Nishida,* Kobe University, Japan

We measured the incident energy dependence of the relative cross section of both elastic scattering and vibrational excitation of methane molecule physisorbed on the surface of Ag(111) using high-resolution electron energy loss spectroscopy (HREELS). The substrate was mounted on a closed-cycle refrigerator attached on a manipulator for XYZ translation and rotation, and is cooled down to 15K. It has been measured that the elastic cross section shows double dips suggesting the existence of surface resonance.@footnote 1@ At the present experiment with improved resolution, the variation of resonance structure was measured depending on the ambient pressure of CH@sub 4@, which possibly corresponds to the variety of the structure of adsorbed CH@sub 4@ . In addition, the shape of the loss peaks in EEL spectra has a tail which might indicate the rotation of CH@sub 4@ molecule on the surface. @FootnoteText@ @footnote 1@ M. Sakurai, T. Okano and Y. Tuzi, Vacuum 41, 234 (1990).

SS3-TuP19 Adsorbate Induced Electronic Relaxation at Transition Metal > Surfaces*, **G. Fahsold**, A. Priebe, M. Sinther, A. Pucci,* Universität Heidelberg, Germany

We investigate the relaxation of electrons at transition metal surfaces by means of IR-spectroscopy. The adsorbate induced relaxation of electrons is responsible for the DC-resistivity of metal thin films, it is connected to the damping of adsorbate motion, and it contributes to enhancement effects observed in adsorbate vibrational spectroscopy. We measured the contribution of adsorbates (CO, O) to the relaxation of electrons at iron and copper surfaces by observing adsorbate induced broadband changes, firstly, in the IR-reflectivity from thick (opague) epitaxial films and, secondly, in the IR-transmission through ultrathin (< 5 nm) smooth epitaxial films. The higher (compared to IRAS measurements) sensitivity for adsorbate resistivity in IR-transmission is well demonstrated by our experimental results. We understand our results on the basis of a proper description of the optical properties of bulk metals and metal thin films. The talk will focus on the importance of the inclusion of non free-electron-like properties for calculating both the magnitude, the sign, and the spectral shape of adsorbate induced broadband effects.

SS3-TuP20 Electron-hole Pair Generation in Adsorption of Gas-phase H(D) Atom on Pt(111) and Cu(111)*, **J.H. Kim**, S.J. Lee, J.S. Choi, J. Lee,* Seoul National University, Korea

Adsorption of gas species at solid surface proceeds via trapping of incident atom(or molecule) in the surface potential well, which requires an energy transfer to the surface. It is generally believed that multi-phonon creation is the dominant mechanism for the energy transfer. However, for the gas-phase H(D) atom, the lightest of all, phonon creation is expected to be negligible because of an extremely poor mass matching, and therefore other loss mechanism such as electron-hole pair creation may be the dominant mechanism.@footnote 1@. We have investigated adsorption on Pt(111) and Cu(111) surfaces at 100K of the gas-phase H(D) atom generated in a hot tungsten capillary tube at 1900K. The hot electrons and holes generated upon adsorption of H(D) atom were detected as an external short-circuit current using metal/n(p)-type Si(100) Schottky diodes. We will compare the results for the two surfaces and interpret in terms of the different electron density of states near the Fermi level. Based on these results, we will also discuss about the widely different sticking probability, saturation coverage, and abstraction reaction probability of H(D) atom on the two surfaces. @FootnoteText@@footnote 1@Nienhaus et al., Phys. Rev. Lett. 82 (1999) 446.

SS3-TuP21 Thermal Accommodation Coefficients Measurement of Inert Gas on Surface of Stainless Steel Sphere*, **B.S. Jun**, T.K Ghosh, R.V. Tompson, S.K Loyalka,* University of Missouri-Columbia

Heat transfer in the fuel-clad gap in a nuclear reactor impacts the overall temperature distribution, stored energy and the mechanical properties of a nuclear fuel rod. Therefore, an accurate estimation of the gap conductance between the UO2 fuel and the clad is critically important for reactor design and operations. To obtain the requisite accuracy in the gap conductance estimation, it is necessary to take into account the thermal accommodation coefficients of the various gases that are involved. This paper summarizes some recent efforts to obtain stainless steel accommodation coefficients experimentally. To get these values, a high-vacuum system was constructed incorporated in tandem a mechanical vacuum pump and a turbo molecular pump. Thermal accommodation coefficients for helium on stainless steel have been obtained by measuring the cooling rates of a stainless steel sphere suspended in the vacuum chamber. The cooling rate in vacuum is measured and subtracted from the cooling rate in helium at various pressures to yield the approximate net cooling rate of the sphere due to molecular impacts. Knowing the heat capacity of the sphere, its net cooling rate, the temperature difference between the sphere and the ambient gas far from the sphere, the pressure, and the rate of impingement of the gas molecules on the surface of the sphere, one can calculate the efficiency of the energy transfer to the impinging molecules. These measurements have been made on so-called engineering surfaces where no special attempt other than standard baking under high vacuum to remove volatile surface contaminants was used to clean the surfaces. It has been found for helium and argon gas that the thermal accommodation coefficient values with stainless steel are quite constant over the range of pressures studied.

SS3-TuP22 Hyperthermal Product Velocity Detected as a Signature of Electron Harpooning in Gas-Surface Reactions*, **G.C. Poon**, J.-C. Gumy, K.A. Pettus, A.C. Kummel,* University of California, San Diego

Multiphoton Ionization (MPI) and Time-of-Flight Mass Spectroscopy (TOF-MS) have been used to demonstrate that the reaction of ICl on the low work function Al(111) surface proceeds by a nonadiabatic electron harpooning process. In the nonadiabatic model of this reaction, as ICl approaches the Al(111) surface, an electron harpoons from the surface, suddenly converting ICl to ICl@super -@. This places the molecule high on the repulsive portion of the ICl@super -@ potential curve leading to rapid dissociation of ICl@super -@ into I@super -@ and Cl fragments. Following this remote dissociation of ICl above the surface, I@super -@ proceeds towards the surface and sticks while Cl is ejected into the gas phase. This is referred to as chemically selective abstraction and is consistent with the observed excess iodine on the surface by Auger Electron Spectroscopy and the detection of ejected Cl atoms. The experimentally observed signature of this harpooning process is the hyperthermal translational energy of the ejected fragment. A harpoon process should give fast Cl whose energy is determined by the vertical transition between ICl and ICl@super -@ and be independent of incident translational energy. Conversely, a conventional adiabatic abstraction reaction should provide only a small translational energy for the ejected Cl and should increase with increased incident translational energy. Hyperthermal Cl (0.36 eV ± 0.14 eV) ejected from the surface has been observed using MPI/TOF-MS, which is evidence for the aforementioned nonadiabatic process. Furthermore, DFT calculations of the vertical transition energy from ICl to ICl@super -@ are in good agreement with experiment. Comparison of the translational energy of ejected Cl from the abstractive chemisorption of Cl@sub 2@ and ICl will also be presented. Cl@sub 2@ should lead to even faster Cl ejected from the surface than for ICl, since Cl@sub 2@@super -@ is formed even higher on the repulsive portion of the potential curve.

SS3-TuP23 Growth Process of Self-organized Ge Quantum Dots on Si(111)-(7x7) Surface Studied by STM*, Y. Zhang, L. Yan, S. Xie, **S. Pang**, H. Gao,* Chinese Academy of Sciences, P.R. China, China

The influence of substrate temperature on the nucleation and self-organized growth of submonolayer Ge on Si(111)-(7x7) surfaces grown by solid phase epitaxy (SPE) has been studied using scanning tunneling microscopy (STM). Ordered Ge quantum dots on the surface are formed through controlling the annealing temperature after submonolayer Ge deposition at room temperature. The formation of ordered Ge quantum dots is due to the preferential adsorption sites of Ge on Si(111)-(7x7). The formed ordered nanostructures may have a potential in the application of nanodevices.

SS3-TuP24 Halogen Adsorption on Pt(110): A Coverage-dependent Charge Density Wave Transition*, **K. Swamy**, C. Deisl, R. Beer, A. Menzel, E. Bertel,* University of Innsbruck, Austria

STM and LEED results of halogen (Cl, Br) adsorption on Pt(110) show a sharp, coverage-dependent phase transition into a charge density wave ground state for a coverage of @THETA@ = 0.5 ML. At this coverage Br orders in a c(2x2) and Cl in a (2x1) structure. The (1x2) missing-row reconstruction of clean Pt(110) is lifted. Contrary to our previously published mode,@footnote 1@ LEED-IV data and ab-initio calculations reveal that the halogens are not substitutionally adsorbed, but in every second short-bridge site.@footnote 2@ Both, the Br-c(2x2) and the Cl-(2x1) phase can be transformed into a (3x1) phase by minute amounts of excess halogens (@THETA@ = (0.5 + @delta@) ML), but also of molecular species (CO and NO). The Br-c(2x2) derived (3x1) phase is stable up to T > 500 K, while the Cl-(2x1) derived (3x1) phase is long-ranged ordered only at T < 200 K. Low-temperature ARUPS spectra prove that the Br-(3x1) and the Cl-(3x1) phases have an almost identical electronic structure. We interpret the (3x1) structure as a charge density wave. This is compatible with the ARUPS data, i. e. we find a corresponding nesting vector and a Peierls gap. @FootnoteText@ @footnote 1@ K. Swamy, A. Menzel, R. Beer, and E. Bertel, Phys. Rev. Lett. 86, (2001) 1299. @footnote 2@ K. Swamy, C. Deisl, E. Bertel, V. Blum, L. Hammer, K. Heinz, C. Franchini, and J. Redinger, in prepration.

SS3-TuP25 A LEED Investigation of Xe Adsorbed on Pd(111)*, **J. Zhu**, H. Ellmer, H. Malissa, D. Semrad, P. Zeppenfeld,* Johannes Kepler Universität Linz, Austria

Xe adsorption on the Pd(111) surface was investigated by means of low energy electron diffraction (LEED) in a UHV chamber with 1.2x10@super -11@ mbar base pressure. Depending on the Xe coverage and substrate temperature, a large number of different phases were identified, including a 2D gas phase and a 2D liquid phase, a commensurate (@sr@3x@sr@3)R30° solid phase (C), a compressed striped incommensurate phase (SI), ordered multilayer structures, and a clear Xe(111) crystal with sharp spots rotated 30° with respect to the substrate. In addition, a hexagonal incommensurate solid phase (HI) and a hexagonal incommensurate rotated phase (HIR) were observed as well as a C -> SI -> HI -> HIR phase transition. The (@sr@7x@sr@7)R19.2° and (@sr@19x@sr@19)R23.5° commensurate phases reported by Hilgers et al.@footnote 1@ were not obtained after Xe adsorption on the clean surface in the entire temperature and coverage range. However, small amounts of contaminants (CO and/or H@sub 2@) on the Pd(111) surface have a striking influence on the Xe post-adsorption. With ~0.1 L of CO pre-adsorbed at 55 K, a clear (@sr@7x@sr@7)R19.2° commensurate phase is obtained. After pre-adsorption of ~0.1 L of H@sub 2@ at 55 K, a commensurate phase (@sr@19x@sr@19)R23.5° appears in the high Xe coverage region. A combination of 0.1 L H@sub 2@ and 0.1 L CO pre-adsorbed at 55 K leads to a phase transition sequence from (@sr@3x@sr@3)R30° -> (@sr@19x@sr@19)R23.5° -> (@sr@7x@sr@7)R19.2° similar to the one reported for Xe on Pd(111) in Ref. 1. From these observations, therefore, we conclude that the high-order commensurate (@sr@7x@sr@7)R19.2° and (@sr@19x@sr@19)R23.5° phases of Xe are related to CO and H@sub 2@ impurities, respectively. @FootnoteText@ @footnote 1@ G. Hilgers, M. Potthoff, N. Müller and U. Heizmann, Surf. Sci. 322 (1995) 207.

SS3-TuP26 Adsorption and Absorption of Hydrogen by Ti(0001): A Study Combining Surface Characterization and Non-destructive H-Depth Profiling*, **M. Wilde**, M. Matsumoto, K. Fukutani, T. Okano,* University of Tokyo, Japan*; Y. Mizuno, T. Homma,* Chiba Institute of Technology, Japan

In the present work the interaction of the Ti(0001) single crystal surface with molecular H@sub 2@ and atomic H is studied at temperatures of 100-300 K. We combine standard UHV techniques of clean surface preparation and characterization with hydrogen depth-profiling by nuclear reaction analysis (NRA, via the @sup 1@H(@sup 15@N,@alpha@@gamma@)@sup 12@C reaction), which allows straightforward assigning of the features in H@sub 2@ thermal desorption spectra (TDS). Molecular H@sub 2@ admitted at T650 K is unaffected. The outgassing rate is characterized by an activation energy in excellent agreement with the heat of H solution in @alpha@-Ti of 21.6 kcal/mole.

Thin Films

Room 134/135 - Session TF-TuP

Microstructure, Oxides, and Optical Properties Poster Session

TF-TuP1 MEVVA Ion-implanted Cr Interlayer on the Microstructure of CrN on Steel*, S. Han,* National Taichung Institute of Technology, R.O.C.*; J.-H. Lin,* National Tsing Hua University, Taiwan, ROC*; Z.C. Chang,* National Chin-Yi Institute of Technology, R.O.C.*; C.J. Yang, F.-S. Shieu,* National Chung Hsing University, R.O.C.*; **H.C. Shih**,* National Tsing Hua University, R.O.C., TAIWAN

The effect of MEVVA ion-implantation of Cr on the microstructure and properties of CrN coatings on the steel were investigated in this paper. Two types of CrN-coated specimens (CrN/steel and CrN/Cr/steel) by cathodic arc plasmas deposition were prepared with and without an interlayer deposited by MEVVA ion-implantation of Cr. And the microstructure and microchemistry of chromium nitride has been investigated by using X-ray diffraction (XRD), cross-sectional transmission electron microscopy (XTEM) and selected area diffraction (SAD). Therefore, the coatings exhibit a microcolumnar morphology. The outermost layer of the coating is identifed as CrN. Furthermore, from an estimation of the unrelaxed thermal stresses based on a bilayer model, it is demonstrated that the presence of a Cr interlayer between CrN and steel can dramatically reduced the thermal stress in the CrN coating.

TF-TuP2 Growth of Wide Band Gap MnS Thin Films by rf Sputtering: Substrate Temperature Effects on Structure and Composition*, S.A. Mayen-Hernandez, R. Perez-Castanedo, **O. Jiménez-Sandoval**, G. Torres-Delgado, S. Jiménez-Sandoval,* Cinvestav-IPN, Mexico

Manganese sulfide (MnS) is a wide band gap semiconductor that crystallizes in its stable form with the octahedrally coordinated rocksalt structure, presenting as well other metastable structures: cubic(zincblend) and hexagonal (wurtzite). One of the problems that have precluded the application of this semiconductor in devices, has been the little work carried out so far to grow high quality MnS films. To date, most of the work done on MnS has been using chemical bath and thermal evaporation as preparation thecniques. These two methods yielded amorphous and polycrystalline films, respectively. To our knowledge, no report exists so far on the growth of MnS films by rf sputtering due to the technical difficulties involved. In this work we report on the appropriate conditions for the growth of nearly stoichiometric MnS thin films prepared by rf sputtering and the important effects of substrate temperature on film composition and structure. The produced films were polycrystalline with an energy band gap of around 3.47 eV, a value that makes MnS an appealing material for optical windows in applications such as solar cells.

TF-TuP3 Structural Investigations for Amorphous Films Deposited by Simultaneous DC Sputtering of ZnO and In@sub 2@O@sub 3@ Targets*, T. Moriga,* ***A. Fukushima****, K. Tominaga, I. Nakabayashi,* The University of Tokushima, Japan

Oxide films in the ZnO-In@sub 2@O@sub 3@ system were deposited by simultaneous dc sputtering of ZnO and In@sub 2@O@sub 3@ facing targets at the substrate temperature of 150°C. The ratio @delta@ of the ZnO target current to the sum of both the currents was varied. In the @delta@ range from about 0.20 up to 0.67, an amorphous film with one broad diffraction peak at around 2@theta@=33° could be deposited. At the higher substrate temperature of 300°C, the crystallized films with the homologous Zn@sub k@In@sub 2@O@sub k+3@ structure (k=2 for @delta@=0.50, k=3 for @delta@=0.57, and k=5 for @delta@=0.67) were deposited in the range from 0.50 to 0.67, and the bixbyite-type In@sub 2@O@sub 3@ phase was observed in the @delta@ range of 0=<@delta@<0.50. We analyzed the peak position of the amorphous films. For example, we took the amorphous film with @delta@=0.50. The broad peak lies in the center of two peaks. One was the (008) peak which appears strongly in the homologous Zn@sub 2@In@sub 2@O@sub 5@ films. The other was the (104) peak which appears strongly in the bulk Zn@sub 2@In@sub 2@O@sub 5@. The amorphous film with @delta@=0.50 had the atomic ratio of Zn:In=1:1. These facts imply that the amorphous film with @delta@=0.50 would be comprised of NOT-ordered Zn@sub 2@In@sub 2@O@sub 5@ matrix. We will discuss a possibility of existence of ZnIn@sub 2@O@sub 4@ (k=1 in Zn@sub k@In@sub 2@O@sub k+3@), by applying this kind of concept to an amorphous films with @delta@=0.33. The @delta@-value dependence of electrical properties (resistivity, carrier concentration and Hall mobility) suggest the existence of ZnIn@sub 2@O@sub 4@.

TF-TuP5 Micro-crystallites in Mo/Si Multilayer EUV Coatings*,* ***E. Louis****, I.J. Wever, A.E. Yakshin, F. Bijkerk,* FOM-Rijnhuizen, The Netherlands*; J. Verhoeven,* FOM-Amolf, The Netherlands*; E. Ziegler,* European Synchrotron Radiation Facility, France

The reflectivity of 13.5 nm radiation by a Mo/Si multilayer system (periodicity 6.7 nm) depends strongly on the interface roughness and the thickness of the interfacial molybdenum-silicide layers. Ideally, the structure of the constituent layers of these Mo/Si coatings is amorphous. In this work we show results of X-ray diffraction experiments that clearly show the presence of small crystallites in the Mo layers, and, depending on the process parameters during the deposition of the layers, in the molybdenum-silicide interlayers. By varying the incident angle and the energy, we were able to observe a preferential orientation of the crystallites. The crystal orientation was found to depend on the various process conditions during the deposition of the layers and ion beam smoothening of the interfaces. We also observed indications of stress in the Mo-crystallites. The results were obtained using Cu-K radiation in an in-house diffractometer (Philips MRD) as well as 16 keV photons at beam line BM5 at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France.

TF-TuP6 Fabrication of Perforated Thin Films with Helical and Chevron Pore Shapes*,* ***K.D. Harris****, M.J. Brett,* University of Alberta, Canada

We will present a simple method for the fabrication of thin films or membranes perforated by helical and chevron shaped pores. Using the glancing angle deposition (GLAD) evaporation technique highly porous (40-50% of bulk density) SiO@sub 2@ thin films of helical and chevron microstructure were deposited on Si substrates. Typical thin films have thicknesses on the order of 2µm and are composed of 1 to 20 turns. The thin films produced by this technique were filled with photoresist and, subsequently, etched to remove the helices, leaving a continuous photoresist cast of the original film. It has been found possible to produce these perforated photoresist films from microstructures distributed either randomly over the substrate, or from structures grown on well defined, periodic arrays of micrometer or sub-micrometer spacings. The perforations have been produced in both chevron and helical shapes, and both photoresist and spin-on-glasses have been successfully used to fill the template. In addition, it has been found possible to electroplate back up through the perforated thin film, reproducing the structure of the original template with an alternate material. The fabrication processes will be discussed along with the results of optical and magnetic characterization of the films.

TF-TuP7 Influence of the Deposition Conditions on the Growth and Structure of Fe Films on Cu(001)*,* ***S.K. Clowes****, L.V. Goncharova, B.J. Hinch,* Rutgers University

We have undertaken an in-depth study into the growth and structure of Fe/Cu(001) films using helium atom scattering, AES and SPA-LEED. This is a system which has been extensively studied during the last two decades, but which has produced a number of contradictory conclusions for the growth mode of the Fe films. This study has paid particular attention to the effects that the specific conditions during deposition have on the growth and quality of the films. These include the rate-of-deposition, surface defects, substrate temperature and contaminants such as oxygen. It is known that oxygen allows the formation of a single, well ordered, monolayer by reducing the surface free energy when it is adsorbed in the fcc hollow site. In a similar manner, it is suggested that under certain conditions oxygen can behave as a surfactant during the deposition of thicker films, promoting layer-by-layer/bilayer growth.

TF-TuP8 Engineering of Porous Thin Films by Modification of Substrate Topography*,* ***B. Dick****, D. Vick,* University of Alberta, Canada*; T. Smy,* Carleton University, Canada*; M.J. Brett,* University of Alberta, Canada

A unique class of evaporated porous thin films has been developed using the technique of glancing angle deposition (GLAD). High porosity in the films is achieved by in situ control of the substrate orientation during deposition. At sub-micron scale lengths, the structure of the films consists of a "forest" of isolated columns that can be engineered into a variety of shapes. For certain envisioned applications, a regular arrangement of uniformly shaped columns may be desirable. Previous work suggests that these requirements may be difficult to achieve on planar substrates due to the column competition, extinction and thickening that occurs during growth of the film. These related phenomena arise from the fact that the advancement of the film - vacuum interface is an inherently non-linear process in which the self-shadowing mechanism plays a predominant role. We are currently investigating the degree to which order may be imposed on the film growth by means pre-patterned substrate topography. Using lithographic and embossing techniques, substrates with patterned seed arrays have been created, onto which GLAD films are then deposited. The elevated seeds serve as nucleation sites for the columns by exploiting the self-shadowing mechanism. After deposition, the films can be analyzed using atomic force and scanning electron imaging, with the dual aim of determining scaling behaviour and identifying appropriate choices of substrate and deposition parameters to produce stable column growth. Results from an experimental study supplemented by 3D-FILMS ballistic simulations will be presented. Recent examples of metal and oxide films deposited by electron beam evaporation and sputtering onto patterned and planar topography will be shown, together with a summary of our present understanding of the growth behaviour of GLAD films.

TF-TuP9 Composite Tantalum Nitride-Silicon Nitride Thin Films for 193nm Embedded Attenuated Phase Shift Masks*,* ***M.G. Lassiter****, M. Cangemi,* Photronics Corporation*; P.D. Rack, B.W. Smith,* Rochester Institute of Technology

As semiconductor device dimensions continually decrease in size, the ability to print these dimensions using 248nm light from a KrF excimer laser is becoming increasingly more difficult. According to Lord Rayleigh's resolution criteria the minimum resolution on the wafer is proportional the exposure wavelength divided by the numerical aperture of the objective lens. Thus resolution can be improved by using smaller wavelengths, which has brought about the development of exposure systems that use the 193nm ArF excimer laser. The use of a new exposure wavelength requires the development of new materials for the photomasks used in such an imaging system. Image contrast has been significantly improved in the past due to the use of embedded attenuated phase shift masks (EAPSM). An EAPSM induces a 180-degree phase shift and limited transmission in the regions that are traditionally opaque in a binary mask. The result is a phase induced contrast enhancement at image edges at the expense of higher background intensity compared to a binary mask. New materials are needed to construct such a mask for 193nm wavelength. This paper explores the use of a composite TaN-Si3N4 for the purpose of providing both the radiation attenuation and the relative phase shift on an EAPSM for use at 193nm wavelength. The TaN and Si3N4 were each reactively rf sputter deposited and their respective optical constant spectra were determined using a Woollam VUV-Variable Angle Spectroscopic Ellipsometer. An effective media approximation (EMA) was used to combine the constituents to tune the optical properties to the desired values for an EAPSM film. Finally, a matrix of composite thin films of varying the TaN-Si3N4 composition were co-deposited and the optical constants of the composites were determined using the ellipsometer to verify the EMA. The composition was iteratively tuned to provide the optimum optical constants at 193nm for a 20% transmission EAPSM.

TF-TuP10 Electrical, Optical and Structural Properties of Sol-gel Deposited Tantalum Oxide Thin Films*, **M.J. Alam**, D.C. Cameron,* Dublin City University, Ireland*; M.S.J. Hashmi,* Dublin City University

Because of its wide field of applications in semiconductor sciences, tantalum oxide (Ta@sub2@O@sub5@) has been extensively studied both experimentally and theoretically over the past three decades. Tantalum oxide films are of considerable interest in optical and optoelectronic technology. Tantalum oxide film is a promising candidate as a capacitor dielectric in high-density dynamic random-access memories (DRAMs) and in ultra-large-scale integrated devices (ULSI) due to its high dielectric constant (about 25) compared with that of only 3.9 for SiO@sub2@. @paragraph@ To date, tantalum oxide films have been deposited using a variety of deposition techniques, such as, thermal oxidation, electron beam evaporation, reactive evaporation, reactive sputtering, pulsed laser deposition and chemical vapor deposition, as well as the sol-gel method. Recently, the preparation of tantalum oxide films by a sol-gel process has received increased attention. This technique has many advantages, such as low temperature processing, simple and compact equipment, deposition on a substrate of large area and a complex structure and high homogeneity of the deposited films. @paragraph@ Thin homogeneous tantalum oxide films have been prepared on silicon and glass substrates using a sol-gel process. The coating solutions were prepared using Ta(OC@sub2@H@sub5@)@sub5@ as a precursor. X-ray diffraction studies determined that the sol-gel films, annealed at temperatures below 400°C were amorphous. Films annealed at higher temperatures were crystalline with the hexagonal structure. X-ray photoelectron spectroscopy was employed to examine the elemental content during the process. Ellipsometry, Fourier transform infrared spectroscopy, capacitance-voltage and current-voltage measurements were also employed to characterize the tantalum oxide films annealed at different temperature in different atmospheres.

TF-TuP11 Infrared Emission from Electroluminescent Thin Film ZnS Doped with Rare Earth Fluorides*, **W. Glass**, A.S. Kale, R. Owing, M.R. Davidson, P.H. Holloway,* University of Florida

Alternating current thin film electroluminescent devices (ACTFELDs) are well-known thin film structures used for flat panel displays. A well-known phosphor for such displays is ZnS doped with either transition or rare earth elements. For example, ZnS:TmF@sub 3@ emits blue light, ZnS:NdF@sub 3@ emits orange, ZnS:DyF@sub 3@ emits yellow, and ZnS:ErF@sub 3@ emits green. Each of these materials also emits in the infrared. The infrared emission from these types of materials is often overlooked except in the case of ErF@sub 3@, which has been of interest for fiber optic communications. The infrared intensity of these materials is dependent on the environment of the luminescent centers and can be improved by modification of deposition and processing. In this study, rare earth fluoride doped ZnS films were deposited by RF planar magnetron sputter deposition or thermal evaporation. Deposition temperature and annealing conditions are varied to determine temperature effects during and after deposition. In addition, the rare earth concentration was changed from a maximum of 1.6 mol% to zero by simultaneously sputtering an undoped ZnS target. The devices were then excited by electroluminescence to determine the effects of the deposition variations. These sputtered devices will be compared to those deposited by evaporation. Finally, emission from materials with similar and dissimilar luminescent decay paths will be discussed.

TF-TuP12 Aluminum Flakes with Enhanced Spectral Properties*, **K.E. Coulter**, R.W. Phillips,* Flex Products, Inc.*; T. Mayer,* Optical Coating Laboratory, Inc.*; R.A. Bradley, J.S. Matteucci,* Flex Products, Inc.

A vacuum deposited multi-layer rigid and brittle bright metal flake has been developed that provides favorable planar specular reflective characteristics in the visible wavelength range and application and durability advantages. Two constructs of the 300nm thick by 15micron in diameter brittle flakes have been demonstrated. One design has a central layer of reflective material supported on both sides by dielectric layers at a thickness of 10-100nm. The addition of the dielectric layers theoretically reduces the specular reflectance of the aluminum surface but the addition a dielectric for support increases reflectance 5-10% in the flake form. The second design utilizes the same materials and dimensions but has the dielectric as the central layer with the reflective material on each side. The result for both designs is a sub-micron thick three-layered metal flake that exhibits a uniaxial compressive strength of approximately 8 times a corresponding uniaxial tensile strength. As a result, the metal flake is then afforded the benefits of rigidity and brittle fracture during manufacturing and application processing. In this talk, a review of design, vacuum deposition processes for manufacture, characterization and use of the flakes in applications will be discussed.

TF-TuP13 The Effect of Annealing upon IR Electroluminescent Emission For Zinc Sulphide: Rare Earth Doped Thin Films*, **A.S. Kale**, W. Glass, R. Owings, M.R. Davidson, P.H. Holloway,* University of Florida

Infrared emitters (IR) enjoy a wide market today with a variety of applications ranging from commercial based fiber optic communication devices to remote controls for televisions. ZnS doped rare earth fluoride thin films typically 1µm thick have been fabricated by RF sputter deposition in the conventional metal-insulator-semiconductor-insulator-metal configuration to study a new structure for IR radiation. The current study investigates three different kinds of phosphors namely ZnS:TmF@sub3@, ZnS:NdF@sub3@ and ZnS:ErF@sub3@ for their IR versus visible emission. Electroluminescence has been investigated after different annealing conditions (as-deposited to 650°C) and time (5-60min), to study the effect on emission properties. As annealing improves the crystallinity of the film, the emission improves. The brightness versus concentration of dopant has been measured and optimized. Emission spectra of the devices have been measured from 0.35 to 1.5µm and the films studied for their emission efficiency and decay time. Methods of enhancing the IR output with respect to the visible have also been studied and reported, including codoping and condition of annealing.

TF-TuP14 Fabrication and Optical Properties of SiO@sub 2@ Sol-gel Made Thin Films Modified with Carminic Acid*, L.L. Diaz-Flores,* Instituto Tecnolodico de Saltillo, Mexico*; G. Luna-Barcenas, J. Gonzalez-Hernandez, **Yu.V. Vorobiev**,* Unidad Queretaro del CINVESTAV-IPN, Mexico

SiO@sub 2@ sol-gel colored films on the glass slides were prepared by traditional process, using the precursor solution made of water, TEOS and ethanol, with the ratio of the components providing good structural quality of the films, and using the dip-coating apparatus. The carminic acid was introduced in the solution; special mechanical treatment of the solution was made to ensure good dispersion of the colorant. The films with intense and stable red color were obtained. The optical absorption spectra of the films contain all three visible absorption bands mentioned in the literature (494, 520 and 555 nm) as well as the UV band at 330 nm not reported earlier. The quantum mechanical description of energy spectrum of the system was attempted based on the modified FEMO approach, treating the carminic acid molecules as three-dimensional quantum wells and using the Born-von Carman boundary conditions corresponding to the mirror reflection of an electron delocalized inside the molecule, from its walls. Good agreement between the theory and experiment was obtained without any adjustable parameters.

TF-TuP15 Inhomogeneous Optical Thin Films and Filters Based on SiN@sub x@:H Prepared by PECVD in Dual-mode Microwave/Radiofrequency Plasma*, **R. Vernhes**, O. Zabeida, J.E. Klemberg-Sapieha, L. Martinu,* Ecole Polytechnique of Montreal, Canada

Deposition of inhomogeneous thin films for optical applications offers great advantages in comparison to traditional multilayer structures. Particularly, optical losses and mechanical stresses due to interfaces are considerably reduced, as well as harmonics and side lobes are eliminated from transmission or reflection spectra. In the present work, we used plasma-enhanced chemical vapor deposition (PECVD) to grow amorphous hydrogenated silicon nitride (SiN@sub x@:H) films on glass and silicon substrates using silane and nitrogen. Control of the refractive index was performed by selectively varying the power of microwave and radiofrequency sources without any change in gas composition. In this way, the film properties are strictly controlled by the energetic interactions in the gas phase and at the exposed surface. The films were characterized by spectrophotometry, variable angle spectroscopic ellipsometry, Fourrier transform infrared spectroscopy, and elastic recoil detection in time-of-flight regime. We found that the radiofrequency mode permits one to obtain a higher refractive index, while the microwave mode leads to a lower refractive index. We demonstrated that this variation was related to a change in composition and density. Indeed, films deposited by radiofrequency mode contain larger quantities of Si-H groups and show a denser microstructure while films grown by microwave mode present a higher concentration of N-H groups with a porous microstructure. We proved that it is possible to pass continuously from one composition and structure to another by gradually adjusting the power of each source. This leads to a continuous variation of refractive index from 1.65 to 1.95. Using this refractive index interval, we demonstrate the fabrication of optical filters with an inhomogeneous refractive index depth profile. Optical and mechanical properties of such filters are discussed.

TF-TuP17 Deposition of Transparent Conductive TiN Oxide Thin Films Doped with Fluorine by PACVD, *F. Arefi-Khonsari,* ENCSP-University of P.M. Curie, France; ***N. Bauduin**, J. Amouroux,* ENSCP-University of P.M. Curie, France

The conductivity of plasma deposited tin oxide films from a mixture of O@sub2@/Ar/Tetramethyltin (TMT) can be enhanced from 0.01 to 100 @ohm@@super@ -1.cm-1 by biasing the substrate by means of a second generator. In this work an attempt has been made to dope the films by a one step process by introducing a fluorine precursor which was SF6 with the plasma mixture used for the deposition of tin oxide films. Optical emission spectroscopy and mass spectrometry were used to study the plasma phase and the characterization of the films was carried out by different surface diagnostic techniques such as SEM, XPS and FTIR. A two fold increase of the electrical conductivity was obtained for very small flow rates of SF6 introduced in the discharge.For higher flow rates, a sharp decrease of the conductivity was obtained. For high flow rates of SF6, competitive etching and functionalization processes assisted by fluorine atoms present in the discharge took place. Although the conductivity dropped down, the optical transmission of the deposited films remained higher than 90%.Moreover, the morphology of the films was modified by the presence of SF6 with an increase of the grain size and the appearance of clusters on the surface of the films.

TF-TuP18 Development of a New Luminescence Spectrum from ZnS:Mn Films, *T. Hirate, N. Orihara, **T. Satoh**,* Kanagawa University, Japan

ZnS Films with a new electroluminescence and photoluminescence spectrum were prepared by the modified chemical vapor deposition method developed by us. The deposition method is a low pressure thermal CVD system basically concerning the synthesis of ZnS matrix except that the metal Mn target is set in the deposition chamber. The two main precursors used to synthesize the ZnS are the metal Zn vapor and H2S. The pulsed Nd:YAG laser beam (wavelength =1.064µm) was used to ablate the Mn target and to dope Mn into the growing ZnS film. The crystal structure of the deposited ZnS:Mn films was analyzed by XRD and the composition was analyzed by EDX and by XPS. The crystallinity of the films was generally poor and it was proven that the deposited ZnS:Mn films consisted only of Zn, S and Mn within the limits of detection by the EDX and XPS analysis. The electroluminescence (EL) spectrum of the ZnS:Mn films hitherto reported has a peak at about 5850Å and the photoluminescence (PL) spectrum has also the main peak at the same wavelength. On the other hand, the EL spectrum of this study has a new peak at 6700Å other than the peak at 5850Å, and the PL spectrum has a strong and wide peak at 7000Å and the intensity at 5850Å is very weak. It was experimentally confirmed that the appearance of these spectra is not due to the concentration of Mn and not due to the interference. We discovered these new spectra and the discrepancy between EL and PL spectrum for the first time. We consider that these may be due to any excited state of Mn generated by the high laser energy density, and that this deposition method has a high probability of development of a new spectrum.

TF-TuP19 Growing Behavior and Luminous Characteristics of ZnGa@sub 2@O@sub 4@ Thin Film Affected by the Substrates and Heat Treatment, *Y.J. Kim, **S.M. Jeong**,* Kyonggi University, Korea*; Y.E. Lee,* ETRI, Korea

ZnGa@sub 2@O@sub 4@:Mn phosphor powder has been well known for the green luminescence for flat panel displays because of its good chemical stability and excellent luminescent properties. However, thin film type ZnGa@sub 2@O@sub 4@:Mn has a limitation in a practical application due to its low luminous properties. In this work, the dependence of growth behaviors and luminous properties on the various substrates and heat treatment were examined. Amorphous, polycrystalline, and highly preferred oriented ZnO thin films were prepared by rf magnetron sputtering method on ITO coated glass substrates to investigate the effects of substrates. Thin film phosphors were deposited on these various substrates, and the structural, luminescent, and optical properties were characterized. It will be emphasized that the structural and luminescent properties of ZnGa@sub 2@O@sub 4@:Mn thin-film phosphors are significantly influenced by the crystallinity of the ZnO layers. On (002) highly oriented ZnO thin film, well developed crystalline ZnGa@sub 2@O@sub 4@thin film could be obtained and showed high luminescent intensity as well. Structural relations between wurzite ZnO film and spinel ZnGa@sub 2@O@sub 4@ film were also investigated to determine the growth mechanism of ZnGa@sub 2@O@sub 4@films. By heat treatment, luminous properties were improved and depended on annealing conditions such as temperature and atmosphere. Defects in as-deposited films which deteriorated the luminous properties could be annihilated by defect transportation and solid state reaction during annealing process.

TF-TuP20 Optical Absorption in the Visible and Near Infrared Range of Electron-beam Deposited Metal-dielectric Structures, ***F. Sabary**, A. de Winne, P. Hamel,* CEA Le Ripault, France

Metal-dielectric structures were deposited by electron beam evaporation. They consist in a silver island film separated from a smooth silver surface by a dielectric material. These structures exhibit strong optical absorptions in the visible range. The spectral position and the amplitude of these absorptions can be modified by changing the mass thickness of the silver island film, the thickness of the dielectric layer and by performing a post-deposition annealing. With appropriate experimental parameters, quasi-total extinction can be obtained. More complex structures have been fabricated by sequential deposition of silver island films and dielectric layers. These structures exhibit a large band absorption in the visible and near infrared range. A theoretical calculation was carried out, based on an effective medium model taking into account the interactions between the silver islands and the metallic substrate.

Tribology

Room 134/135 - Session TR+MM-TuP

Poster Session

TR+MM-TuP2 Investigations on Anisotropic Friction Factor, ***V.V. Tarasov**, A.V. Trubachev,* Institute of Applied Mechanics of Ural Branch RAS, Russia

The anisotropy effect is caused by the difference in the microgeometry characteristics of the surface and its physico-mechanical properties, depending on the direction of tracks of a tool, left after mechanical processing of the surface. In the common case in the presence of the anisotropic friction, in contrast to the isotropic one, the body moves at a certain angle to the direction of the application of the disturbing (imposed) force. With the orthotropic friction (M. Guber) there are two directions on the surface of the body; when the isotropic body is moving in these directions it is possible to know maximal and minimal values of friction coefficient, respectively. We place the axes X and Y in these directions, and designate the corresponding friction coefficients as Đš and k. The mathematical model was suggested for description of the body motion due to anisotropic friction for the constituents of the friction force along the axes X and Y. At the report the a mechanical simulation model is schematically presented for visual study of the peculiarities of friction and motion of the couple of bodies "anisotropic - isotropic surface". For real pairs of friction are more then 0.6, and technologically it is difficult to realize its further decrease. The appearance of the materials with controlled friction characteristics will allow better use of the properties of anisotropic friction in various tribo-conjuctions. The experiments, conducted with the use of the mechanical model, have confirmed both qualitative and quantitative correspondence of experimental and calculated results. The experiments with the use of special samples were carried out for the pairs "isotropic - anisotropic surface" without lubricant. Thus, when the steel plate was used for the experiment, the limiting coefficients were determined: from 0.123 to 0.005. The experiments with the use of special samples were carried out for the pairs "isotropic - anisotropic surface" without lubricant.

TR+MM-TuP3 Friction Properties of Cobalt-based Diamond Materials under Metallic Sliders, ***A.S. Alwatban**,* Riyadh Technical College, Saudi Arabia

The frictional properties of cobalt based diamond containing different size of diamond particles both in air and in vacuum were studied. In both cases a group of a metallic sliders were used. The coefficients of friction tend to increase with the increasing of the diamond particle size. The coefficient of friction in air is lower than that in vacuum. As a results of increasing the number of traversals, significant wear of the diamond composites by metallic sliders (stainless steel) was observed although the coefficient of friction was decreasing. Scanning electron microscopy studies revealed the wear track that and the wear debris formed during the friction tests. One of the significant factors for the reduction of friction could be the embedded fragmented diamond particle in the metallic sliders.

TR+MM-TuP4 Measurement of Rolling Friction for MEMS Applications*, T.-W. Lin, D. Wendland, B. Shapiro, R. Ghodssi,* University of Maryland

Friction has been a major concern in addressing MEMS reliability. The friction force is expected to be less when only rolling friction exists between two relatively moving components in MEMS devices. This concept is examined by a proposed experimental system using 300 µm diameter ball bearings to characterize static and dynamic rolling friction. The system consists of a servomotor, linkages, a platform, sliding rails, a CCD camera, and silicon specimen. The motor combined with the linkages provides the platform with a linear oscillating motion. A silicon plate (stator), 1cm*1cm*500µm, attached on the platform, has two parallel micromachined v-grooves on its top surface. Equal numbers of stainless steel micro-balls are placed in each of the v-grooves. Another silicon plate (slider), identical to the stator, rests on the micro-balls. The gap between two plates is designed to be 3 µm. The micro-balls are in contact only with the walls of the stator and slider v-grooves. The rolling friction at the contact points causes the slider to move along the direction of oscillation of the stator. The camera is used to record the slider's positions over time to determine velocity and acceleration of the slider. The dynamic coefficient of friction is computed by dividing the acceleration of the slider with the acceleration due to gravity. A curve for the instantaneous coefficient of friction is derived. Preliminary results for rolling friction of micromachined silicon surfaces in contact with stainless steel micro-balls will be presented.

TR+MM-TuP5 Tribological Analysis of PET is blendas PET-PMMA for Test Pino-on-disk the Dry*, M.S.B.P. Santos,* CETEC, Brazil, Brasil*; F.J.B. Pinto, **J.R.T. Branco**,* CETEC, Brazil

The concern with the environment preservation has demanded increasing effort to recycle plastics. In a previous investigation we have reported the possibility to manufacture thermal sprayed coatings from recycled PET. Pin-on-disc data demonstrated that coatings had even better wear behavior than virgin PET. In the present work we have investigated the effects of PMMA content on the pin-on-disc and scratching behavior of PET-PMMA blends, in dry condition. AISI 52100 steel 6 mm balls, with and without TiN coatings were used as counterbody. The pin-on-disc wear testing were carried out under 1 and 10 N load. The scratching was performed with 1, 10, 50 and 100 N. Friction coefficient, volume and mass loss were monitored during testing. The paper also investigates on the effect of sliding speed.

TR+MM-TuP6 Nanomechanical Response of Ultra High Molecular Weight Polyethylene Nanostructure*, **L. Riester**,* Oak Ridge National Laboratory*; S.P. Ho, T. Boland, M. LaBerge,* Clemson University

Over the past three decades studies on patients with total joint replacement (TJR) prosthesis have shown that ultra high molecular weight polyethylene (UHMWPE) nanoscale wear debris causes osteolysis leading to subsequent aseptic loosening of the implant and total failure of the implant. At the nanoscale, UHMWPE is a semicrystalline material defined by a crystalline domain within an amorphous matrix. Previous work focused on determining the average mechanical properties assuming isotropy within the material proved insufficient for the consideration of failure analysis due to its composite-like anisotropic nanostructure. While several factors can influence the mechanical failure of a material, this study is limited to investigating the mechanical response of the nanostructure of UHMWPE insert in TJR prosthesis. In this study, the effects of sample preparation technique on the nanostructure and the nanomechanical response of compression molded UHMWPE nanostructure were investigated The nanostructure of UHMWPE samples prepared by ultramicrotoming, cryo-ultramicrotoming and etching techniques was studied using an atomic force microscope. The nanomechanical response of the nanostructure as a function of the sample preparation technique was studied using a Nanoindenter II with a diamond Berkovich indenter tip. The samples were indented using continuos stiffness method at a constant displacement rate for penetration depth range of 50-1000 nanometers respectively. This study shows that sample preparation techniques possibly introduced artifacts as illustrated by the changes in the morphology of UHMWPE, which was especially evident in polymers that were ultrasectioned above their glass transition temperature. It was also shown that the technique of etching a sample surface with a permanganate etchant to reveal the crystalline regions changed the neighboring boundary conditions, which in turn redefined the crystalline nanomechanical response to mechanical loading.

TR+MM-TuP7 Single-Asperity Nanotribology and Nanorheology of Thin Poly(dimethylsiloxane) Films*, **S. Tan**, G. Haugstad, W.L. Gladfelter,* University of Minnesota

The lubricating and non-stick characteristics of poly(dimethylsiloxane) (PDMS) have been exploited for years. As with many tribological systems, technological application led scientific understanding: experimental methods were not available to precisely control intersurface separation, contact geometry and loading conditions about individual surface asperities. In the last 15 years analytical tools have become available for this purpose. Uniquely, scanning force microscopy (SFM or AFM) employs a single microasperity and feedback-actuated tracking of surface topography. Thus "nanotribologists" now can investigate the fundamental unit of tribological systems: a single asperity with measurable radius of curvature, deforming into a material under measurable load, and sliding tangentially to the surface. Many SFM studies have involved simple systems, e.g. clean single-crystal inorganic surfaces or ordered ultrathin organic films lubricating such surfaces. Relatively little work has been on higher molecular weight, disordered films ranging in thickness from boundary lubrication (extremely thin) to bulk hydrodynamic (very thick). Yet real technological systems span this range. In the present work, SFM was employed to study nanotribology and nanorheology on poly(dimethylsiloxane) films varying from several to hundreds of nanometers thick. A wide range of molecular weights was examined, corresponding to bulk viscosities from 350 to 1,000,000 cS. Friction and pull-off forces were found to increase as a small fractional power of velocity over several decades. Similar, scaled-up behavior was observed using a cantilever-attached microsphere (R=10,000 nm) in place of the usual tip (R~10 nm). A dramatic increase in friction and adhesion was observed above a critical film thickness of approximately 3 Rg. Accompanying this increase was a qualitative signature of liquid-like behavior seen in force-versus-distance measurements.

TR+MM-TuP8 Nanowear Patterning as an Activated Crazing Process*, **R.H. Schmidt**,* Lund University, Sweden*; G. Haugstad, W.L. Gladfelter,* University of Minnesota

The friction and wear characteristics of nanoscale organic coatings are critical to new and emerging technologies (e.g. microelectromechanical devices). Fortunately the need to understand this behavior has coincided with the development of tools to measure shear forces on the nanometer scale, including the scanning force microscope (SFM). At the scientific frontier these methods have enabled careful studies of confinement effects on polymer dynamics, e.g. the glass transition. In contrast to traditional scientific disciplines like condensed matter physics and physical chemistry, the nanotribology community has only begun to examine the role of temperature in material response. The response of "soft" condensed matter to external forces can be dominated by entropic (temperature dependent) effects; further, nonequilibrium molecular conformations may introduce kinetic (rate dependent) effects. Rigorous studies of thin-film polymer nanotribology therefore must include methodologies to quantify the interrelated roles of temperature and rate. In the present work, wear on polystyrene films was studied via the commonly observed surface-patterning phenomenon, induced by raster scanning. This was examined in detail as a function of load, scan history (repetitions), scan line density, scan velocity, and temperature (40-115 ºC). Film response was highly linear with respect to load and the number of successive visits of the sliding tip. Results suggest that the scanning process induces damage in the film analogous to crazing in brittle bulk polymers. The temperature and rate dependences were analyzed within the Bingham-Voigt-Arrhenius model of plastic flow. Activation energies extracted from (a) surface roughening and (b) the spacing between scan-induced "bundles", were intermediate to known values for alpha and beta relaxations in the bulk polymer.

TR+MM-TuP9 Decrease in Friction Force of Type 304 Stainless Steel in a Vacuum by Surface Roughness Modification*, **A. Kasahara**, M. Goto, M. Tosa, K. Yoshihara,* National Institute for Materials Science, Japan

Surface modification of sliding motion materials is inevitable to reduce friction as well as outgassing in a vacuum. We therefore study the development of advanced vacuum motion materials by control of surface roughness on a submicron scale. The friction measurement was carried out on typical vacuum material as type 304 austenitic stainless steel sheet with such surface treatments as chemical polishing or electrochemical buffing after mechanical polishing. A frictional probe is a mechanically polished stainless steel ball of 3.18mm in diameter and was slided under load of

0.49N on surface of sheets with surface roughness from 40nm to 1000nm. Friction measurement in an atmospheric pressure showed little change in friction coefficients of sheets with chemical polishing or electrochemical buffing even by changing surface roughness, while friction measurement at the pressure of 1E-6Pa showed that friction coefficients of sheets increased largely except those of sheets with surface roughness around 100nm prepared by chemical polishing or electrochemical buffing. Stainless steel sheets modified only with surface roughness around 100nm can keep low friction coefficient of 0.1 both in an atmospheric pressure and in a high vacuum, which will help smooth sliding motion required for vacuum system.

TR+MM-TuP10 Friction Behavior of Third Element Incorporated Diamond Like Carbon Films in Various Environments*, S.J. Park,* Korea Institute of Science and Technology*; K.-R. Lee,* Korea Institute of Science and Technology, Korea*; K.Y. Eun,* Korea Institute of Science and Technology*; A. Scholl, F. Nolting, A. Padmore,* Lawrence Berkeley National Laboratory*; D.-H. Ko,* Yonsei University, Korea

Tribological reaction between the steel ball and third element incorporated diamond-like carbon(DLC) film was investigated from the view point of tribochemical reaction. Si and W was selected for third element. Si incorporated DLC films were deposited using r.f. PA-CVD with mixtures of benzene and diluted silane gases. And W incorporated DLC films were deposited using hybrid DC magnetron sputtering system with methane and Ar. Si(100) wafer was used for substrate. Tribological test was performed using ball on disk type wear-rig. AISI52100 steel ball was used for the wear test. The test environments were dry air, humid air, and vacuum. In the case of the Si incorporated DLC film, it was observed that the debris were partly polymerized and finely dispersed when the Si concentration was larger than 5 at.%, which resulted in low and stable friction behavior in humid air. In dry air, the chemical bond structure of the debris was essentially the same as those in humid air. However, the debris of smaller size has more spherical shape. But in vacuum the debris at low Si concentration showed typical NEXAFS spectrum of a polymer. The polymeric component in the debris decreased as the Si concentration increased In W incorporated DLC films, it has lower friction coefficient but higher wear rate than a-C:H films made by PA-CVD. By analysis of the composition of debris, its friction behaviors were closely related to the formation of the silicon-rich oxide debris.

TR+MM-TuP11 Structure Analysis of Tetrahedral Amorphous Carbon Films using Synchrotron Radiation Light Source*, C.S. Lee,* Korea Institute of Science and Technology*; K.-R. Lee,* Korea Institute of Science and Technology, Korea*; K.Y. Eun,* Korea Institute of Science and Technology*; K.H. Yoon,* Yonsei University, Korea

Using energetic condensation of carbon ions from filtered vacuum arc plasma, tetrahedral amorphous carbon (ta-C) films were deposited on Si (100) wafers. During the deposition, a dc bias voltage ranging from 0 to -500V was applied to obtain films with various atomic-bond structures. Mechanical properties of ta-C films show the strong dependency on applied bias. The change of the atomic bond structure in ta-C film was analyzed by near edge x-ray absorption fine structure (NEXAFS). In the present work, we focused on the changes in NEXAFS spectrum in various deposition condition and post annealing processes. The relationship between peaks observed in the spectrum and the structural change in the film was identified in the conjunction with Raman and electron paramagnetic resonance spectroscopy (EPR). Based on these results, the suggested models on the atomic bond structure of ta-C film will be discussed.

TR+MM-TuP12 Effects of Metal Dopant Content on Mechanical Properties of Ti-Me-N Films*, H.K. Park,* Sungkyunkwan University, Korea, South Korea

TiN coatings was applied for various application fields, because of a good wear-resistance and a high hardness. Typically, TiN thin films shows the hardness of 2200 kgf/mm@super 2@ and friction coefficient of 0.6. However, in many field, one is looking for a more improved tool which has low friction coefficient and high wear resistance. The main motivation of this study is to characterize the influence of various metal dopant content on TiN thin films. Ti-Me-N thin films were deposited onto steel substrates by PVD processing with a Ti target and various metal target. In this work, we synthesized titanium nitride films similar with reported typical titanium nitride films and synthesized Ti-Cu-N thin films with the addition of elemental copper which is measured improved hardness more than pure TiN films with copper content variables. This films has preferred oriented films of (111) direction. In addition, It was found that there is a strong correlation between content of various metal and film characteristics such as preferred orientation, grain size, hardness, and friction coefficient and so, in future study, improved mechanical properties of TiN films can be controlled and changed by selection and content of elements such as Sn and Ag modifying the film. The Ti-Me-N film will show apparent hardness characteristics and mechanical properties enhancement, when doping element is added onto TiN thin films. Film structure, chemical composition, mechanical properties were investigated by means of X-ray diffraction(XRD), scanning electron microscopy, X-ray photoelectron spectroscopy, wear resistance tester, hardness tester.

Applied Surface Analysis
Room 134 - Session AS-WeM

Biomaterials and Polymers

Moderators: D.H. Fairbrother, Johns Hopkins University, S.L. McArthur, University of Washington

8:20am **AS-WeM1 Surface Characterization of Biomaterials for Medical Applications*, H.J. Mathieu,*** Swiss Federal Institute of Technology Lausanne (EPFL), Switzerland **INVITED**

Biomaterials are non viable materials used as medical devices interacting with biological systems and are increasingly being applied as substitutes and/or sensors in human hosts. This paper describes the specific surface functionalization and characterization of biomaterials for Medical Applications by use of methods such as x-ray photoelectron spectroscopy (XPS) and imaging time-of-flight secondary ion mass spectrometry (ToF-SIMS) as well as contact angle measurements and scanning force microscopies (SFM). Bio-molecules (peptides, polysaccharides, proteins, etc) are grafted to various types of materials ranging from metals, semiconductors to polymers. It is the bulk composition which determines the physical, mechanical and rheological properties, whereas surface chemistry and topography influence the response to a foreign implant. The control of chemistry, forces and topography of surfaces and thin films with femtomol sensitivity, nanometer in-depth information and submicron lateral resolution will be highlighted. Practical applications cover photo-grafting of hydrocarbons for the development of bio-sensors - glycoengineering -, plasma modification of polymers to reduce bacterial adhesion on endotracheal devices and cell adhesion on metallic surfaces. References: 1. D. Leonard and H.J. Mathieu, Fresenius' Journal Analytical Chemistry 365 (1999) 3-11 2. H. J. Mathieu, Surface and Interface Analysis 32 (2001) in print.

9:00am **AS-WeM3 Micromechanical Properties of 'Smart' Gels: A Study of PNIPAAm by Scanning Force and Scanning Electron Microscopy*, T.R. Matzelle,*** Universite Libre de Bruxelles, Belgium*; R. Reichelt,* University of Muenster, Germany*; N. Kruse,* Universite Libre de Bruxelles, Belgium

PNIPAAm [poly-(N-isopropylacrylamide)] is one of the most interesting and promising 'smart' gels. It undergoes a reversible phase transition in response to external temperature changes. The PNIPAAm matrix, swollen in aqueous solution, collapses as the temperature is increased above the lower critical solution temperature (LCST), which is about 33°C. Due to this thermoresponsive ability, these gels are promising candidates for thermal switches, micro/nanoactuators or controlled-release systems. In order to provide information on the local structural and mechanical properties of PNIPAAm we employed scanning force microscopy (SFM) in air or in water at various temperatures below and above the LTSC. SFM images of the gel surface were compared with those obtained in dry, swollen, and collapsed states using field emission scanning electron microscopy (FESEM). Images of SFM and FESEM of the dry hydrogel surface revealed similar structural features. The surface is rather smooth except for small spherically shaped protrusions with a diameter and a height ranging from 10 to 50 nm and from 5 to 15 nm, respectively. FESEM of a cryogenically dried PNIPAAm sample swollen in water at 20°C revealed a coral-like structure with cavities of @tdA@40 nm. Force vs. cantilever displacement curves were measured with both, spherical (µmm-sized) and commercial probes. Indentation of the hydrogel surface as a function of the probe load was evaluated using the Hertz model to determine the local elastic moduli at different temperatures. For the swollen state at 10°C Young's modulus was found to be 1.11 kPa, which is more than 100 times lower than for the collapsed state at 35°C. More generally, this modulus is significantly lower than the moduli measured for biological cells.

9:40am **AS-WeM5 Tailored Polymer Surfaces Controlled by XPS*, J.-J. Pireaux,*** Facultés Universitaires Notre-Dame de la Paix, Belgium **INVITED**

If polymer materials are now so widely used that it is hard to imagine life without them - billions of kilograms of plastics are sold every year-, a significant set of applications rests on polymers in juxtaposition with another material, as in composites or (multi)layered structures. All properties of these ensembles depend on successful and controlled adhesion, a very complex technology indeed that encompasses various physico-chemical interactions between two surfaces. This presentation will review the different methods used in the laboratory, or at the production plant, to modify, if possible in a very controlled way, a polymer surface. To remove superficial contamination, to modify surface morphology, to tune hydrophobicity, to functionalize a polymer surface ... can be achieved by various chemical or physical methods. Surface treatment is particularly versatile when using a plasma discharge, a vacuum technique, while X-Ray Photoelectron Spectroscopy (XPS) appears a method of choice to control the tailored polymer surface. Potentials of the cold (reactive) plasma treatment will be shown; advantages and problems of the XPS characterization method will be pointed out; complementary information gained by FT-infrared and contact angle measurements will be illustrated. Two sample cases will be commented on: (1) plasma treatment of polyester, in various reactive gases that shows ageing (surface oxidized species slowly disappear with time), while an optimum amount of functionalization allows better adhesion of an evaporated aluminium layer (mechanical adhesion test); (2) some parameters governing the physico-chemical interactions at the SiO@sub x@ -functionalized polypropylene interface will be explained with the help of the acid-base concept.

10:20am **AS-WeM7 Synthesis and Characterization of Poly(imidesiloxane) Copolymers Containing Two Siloxane Segment Lengths: Surface Composition and Its Role in Adhesion*, C.M. Mahoney,*** State University of New York at Buffalo*; J.C. Rosenfeld,* Occidental Chemical Corporation*; J.A. Gardella, Jr.,* State University of New York at Buffalo

Polyimidesiloxane (SIM) copolymers are extremely important materials for microelectronic applications due to their excellent adhesive properties, low dielectric constants and good overall thermal and mechanical properties. Hence it is of importance to study the surface and interfacial properties of this polymer system. A series of poly(imidesiloxane) (SIM) copolymers have been synthesized, where the total composition of PDMS was maintained at 10% (by weight) with two different PDMS segment lengths of different relative composition. (e.g. 5% PDMS containing 1 repeat unit, designated G-1 and 5% PDMS containing 9 repeat units, designated G-9 incorporated into the same polymer vs. 1% G-1 and 9% G-9 in the same polymer). Two main polymer series were synthesized, one containing G-1 and G-9 in varying ratios, and the other containing G-5 and G-9. Both of these series have been analyzed using angle dependent X-Ray Photoelectron Spectroscopy (XPS). The results suggest that there is preferential segregation of longer siloxane segment lengths to the surface. The angle dependent data was then used to obtain an in-depth profile by using a deconvolution process. From the profiles, it was determined that the thickness of the surface PDMS layer of all polymers containing both G-9 and G-1 were the same for all compositions studied, while that of the pure 10% G-1 was much less. The adhesion strengths of these polymers were measured using peel strength tests and the adhesion values were correlated to the XPS results. It was found that the adhesion of the pure 10% G-1 was much higher than that of any other polymer in the series. The remainder of the polymers in the series all had similar adhesion values. These results are consistent with a model of the surface, which has longer segment lengths preferentially segregating and dominating the adhesive properties.

10:40am **AS-WeM8 Phase Contrast AFM Analysis of Polymers: Use of Correlative Classification Methods for Phase Identification*, J. Farrar*[1]**, *K. Artyushkova, J.E. Fulghum,* Kent State University

Phase contrast AFM is increasingly utilized in the analysis of polymers and polymer blends. The phase contrast images potentially contain chemical information, although image interpretation can be challenging. In this study we evaluate methods for the correlation of XPS and AFM data, in order to facilitate chemical interpretation of phase contrast AFM images. Polymer grids are used to evaluate the image pre-processing required before the application of classification methods. Processing for image correlation includes resizing, image alignment and resolution matching. Considerations specific to each technique will also be discussed. Following the image processing, classification methods are used to correlate components present in the XPS and AFM images. After validating the approach on test samples, heterogeneous polymer blends are analyzed using image classification methods. This work has been partially supported by NSF ALCOM (DMR89-20147).

11:00am **AS-WeM9 A Surface Chemistry Study of Laser Ablated Polymers Used for Microfluidic Devices*, D.L. Pugmire,*** *E.A. Waddell, C.J. Taylor, L.E. Locascio, M.J. Tarlov,* National Institute of Standards and Technology

Polymer substrates are being investigated for use in microfluidic devices because of their low cost, ease of fabrication, and wide range of materials properties. It is well established that the surface chemistry of a plastic substrate greatly influences the electroosmotic flow (EOF) behavior of microfluidic channels made from that material. Typical channel imprinting techniques do not offer direct control of surface chemistry. Laser ablation

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[1] **ASSD Student Poster Competition Participant**

shows promise as a versatile method for directly forming a variety of microchannel geometries in plastics. In addition, we have demonstrated that surface chemistry, and, therefore, EOF behavior can be controlled by changing the atmosphere under which laser ablation of the plastic is performed. The surfaces of several plastics ablated in a variety of environments were studied with x-ray photoelectron spectroscopy (XPS), attenuated total reflection infrared spectroscopy (ATR-IR), and scanning electron microscopy (SEM). XPS results indicate that laser ablation generally resulted in an increase in the oxygen content of the polymers studied, regardless of ablation atmosphere. However, this oxygen uptake was often more pronounced when ablation was performed under O@sub 2@ as opposed to N@sub 2@ or Ar. Ablation of commercially obtained PVC, with an organotin stabilizer, resulted in concentration of tin species at the ablated surface. These results will be discussed and compared to EOF rates of ablated microchannels.

11:20am **AS-WeM10 RBS-based Characterization of Hyper-Thin Silicon Compound Deposits on Polymers***, **G. Dennler,*** Ecole Polytechnique de Montreal, Canada*; A. Houdayer,* University of Montreal, Canada*; Y. Ségui,* Université Paul Sabatier, France*; M.R. Wertheimer,* Ecole Polytechnique of Montreal, Canada

Rutherford Backscattering Spectroscopy (RBS) with 1 and 1.5 MeV alpha particles has been used to investigate the growth of SiO@sub 2@ and Si@sub 3@N@sub 4@ films deposited by Plasma-Enhanced Chemical Vapor Deposition (PECVD) on three different polymers, namely polyimide, polyethyleneterephthalate and polycarbonate. The thicknesses of the various films considered in this work vary from 0.1 to 50 nm. In the case of Kapton PI, using the IBM geometry at 150°, we verified that the ratio of Silicon to Carbon does not change during irradiation; this signifies that the specimen does not suffer a significant amount of damage. Thus, using this RBS geometry, we were able to follow the surface density of Si atoms versus time of deposition, t, that is, to measure film thickness, d, down to 1 Å. The calibration of d was accomplished using thicker samples, characterized by Variable Angle Spectroscopic Ellipsometry (VASE) and X-Ray Fluorescence (XRF); a perfectly linear relationship between d and t was observed over the entire range, for both coating types on PI. RBS was also used at near-grazing angle (95°) to investigate the interphase between SiO@sub 2@ and polymeric substrates. RUMP simulations predicted a precision of about 5 nm under these conditions. Thus, we investigated a 50 nm SiO@sub 2@ film on Kapton PI and found that the interphase thickness does not exceed 7 nm. The same methods, applied to deposits on the other two polymers, were unsuccessful because of serious modifications of the polymeric substrate, induced by the incident ion beam, even under conditions of very low beam current (1nA) : Scanning Electron Microscopy (SEM) allowed us to observe the damage caused at the surface by the volatile molecular fragments created in the irradiated bulk of the polymer during their escape through the coated sample surface. This work shows clearly that an interphase of the order of 5 nm can be observed in certain cases, but that this IBA technique is not generally applicable for all polymers, because of radiation damage.

Biomaterials
Room 102 - Session BI+SS-WeM
Biological Interface & Surface Science

Moderator: C. Wöll, Ruhr-University Bochum, Germany

8:20am **BI+SS-WeM1 Hybridization Reactions between Surface Attached Oligonucleotides and Complements from Solution***, **W. Knoll,** D. Kambhampati, T. Neumann, M. Chen,* Max-Planck-Institut für Polymerforschung, Germany **INVITED**

The quantitative evaluation of hybridization reactions between surface-attached 15mer oligonucleotides and their complements from solution will be described. Reaction kinetics, as well as equilibrium binding studies are conducted in order to reveal the association/dissociation mechanism. Different strategies to prepare the interfacial probe layers are tested and compared to each other: These are 1) direct coupling of the catcher oligonucleotides to a gold substrate by thiol groups, 2) a streptavidin monolayer-based coupling scheme via biotinylated probe oligos, 3) a similar approach but based on a commercial dextran-streptavidin structure, 4) 15mers attached to polymer brushes grown by a "grafting-from" approach, and finally 5) a layer prepared by electropolymerization of hydroxyphenol-derivatized oligonucleotides. In cases where surface plasmon spectroscopy was not sensitive enough for label-free detection of the hybridization we employed our recently developed surface-plasmon field-enhanced fluorescence spectroscopy. Different versions based on having either the catcher strand labeled, or the target, or both (e.g., for energy transfer studies) will be discussed. Parameters that are studied include the effect of temperature, ionic strength, mismatch (number of bases, position) length of complement, charge density (DNA versus PNA) etc.

9:00am **BI+SS-WeM3 Functionalization of Metal-Oxide-Based Biomaterials and Biosensor Surfaces by Molecular Self-Asssembly Processes***, **M. Textor**, S. Tosatti, M. Zwahlen, S. Finken, J.A Hubbell, G. Haehner,* Swiss Federal Institute of Technology (ETH), Switzerland

Modifications of metal oxide surfaces based on spontaneous adsorption of alkane phosphates and polycationic copolymers and subsequent film formation are shown to be potentially very useful for designing the chemical and biochemical properties of metallic implants and optical biosensors. Alkane phosphates were found to self-assemble on a number of transition metal surfaces such as titanium oxide, tantalum oxide and niobium oxide through direct coordination of the phosphate head group to high-valency metal cations. The chemical and structural properties of the adlayers were investigated using XPS, ToF-SIMS and NEXAFS. Introducing terminal functionalities other than methyl, e.g. hydroxy, amine or oligo(ethylene oxide) groups, allows one to tailor physico-chemical properties such as wettability, surface charge or the strength of protein-surface interactions. A second class of molecular assembly systems, PEG-grafted polycationic copolymers, spontaneously form monomolecular adlayers on negatively charged metal oxide surfaces, imposing high resistance towards biomolecule adsorption. Through further functionalization of the PEG-chains with biotin or peptide moieties, specific interactions of the treated oxide surface with streptavidin or with cell receptors can be induced while preserving the low degree of non-specific events. w-functionalized alkane phosphate SAMs, as well as peptide-modified PEG-grafted copolymers have been applied to both smooth and rough titanium surfaces to produce model surfaces for the study of fibroblast and osteoblast cell-surface interactions, with independent control of surface topography and chemistry. Furthermore, the two novel molecular assembly systems are shown to have a substantial potential for the reproducible and cost-effective modification of chips in optical-waveguide-based bioaffinity sensing of proteins and of DNA/RNA, including their application to microarray-type sensor surfaces.

9:20am **BI+SS-WeM4 Buildup Mechanism for Hyaluronic Acid/polysine Films onto a Solid Interface***, C. Picart, Ph. Lavalle, F.J.G. Cuisinier,* INSERM U424, France*; P. Schaaf,* Institut Charles Sadron (CNRS) Strasbourg, France*;* ***J.C. Voegel,*** INSERM U424, France

The formation of a new kind of biocompatible films based on Poly-L-Lysine and Hyaluronic Acid (PLL/HA) by alternate deposition of PLL and HA was investigated. It is shown that the driving force of the buildup process appears, as for "convential" polyelectrolyte multilayer systems, to be the alternate overcompensation of the surface charge after each PLL and HA deposition. The construction of (PLL/HA) films appears to take place over two buildup regimes. The first regime is characterized by the formation of isolated islands dispersed on the surface and which grow both by addition of new polyelectrolytes on their top and by mutual coalescence of the islands. The second regime sets in once a continuous film is formed at the after the 8th bilayer deposition in our working conditions. QCM measurements at different frequencies evidences a viscoelastic behavior of the films which have a shear viscosity of the order of 0.1 Pa.s. During this second regime the mass of the multilayer film increases in an exponential rather than in a linear way. This exponential growth is explained the diffusion of free PLL chains into the interior of the film when it is brought in contact with a PLL solution and by the diffusion out of the film of a fraction of these free chain followed by their interactions with HA chains at the outer limit of the multilayer when the film is further brought in contact with a HA solution. The diffusion of free PLL chains into the film is also found to be accompanied by an expulsion of water out of the film. This new kind of biocompatible film incorporating a natural polymer of the extracellular matrix and a widely used polypeptide makes it a potential candidate for cell-targeted action and for the coating of different types of surfaces, such as implants or capsules, in order to mimic a natural extracellular gel.

9:40am **BI+SS-WeM5 Orientational Effects and Surface Free Energies in the Amino Acids Adsorption Process onto Silicon-based Surfaces***, G.L. Gambino,* ***C. Satriano****, G. Marletta,* University of Catania, Italy

The present paper deals with the study of the adsorption process of Lysine (Lys) and Cysteine (Cys) from aqueous solutions as a function of the substrate structure and solutions pH. The substrate effect has been studied for three silicon-based substrates, i.e. silicon dioxide, poly(hydroxymethyl)siloxane (PHMS) and oxygen plasma-treated PHMS. The pH role on the adsorption process has been investigated by performing the incubations in the amino acid solutions both at their isoelectric pH and at the physiological pH, i.e. pH = 7.4. The in situ characterization of the substrates-amino acids molecules interaction was performed by means of the Quartz Crystal Microbalance with Dissipation (QCM-D) technique. On the other hand, ex-situ measurements were performed by means of Angular Resolved X-Ray Photoelectron Spectroscopy (ARXPS) and Contact Angle (CA) measurements. In particular, ARXPS, by varying the sampling depth from @tdA@10 nm to @tdA@2 nm, allowed to elaborate a coverage model, while the CA technique, by using three test liquids, allowed to calculate the surface free energies and their relative dispersive and acid-base contributions. QCM-D data shows that Lys and Cys strongly adsorb onto the plasma-treated PHMS while on the untreated PHMS surfaces the adsorption of both amino acids does not occur. ARXPS measurements indicate that the adsorbed molecules exhibit a preferential orientation respect to the plane of the surface, however no uniform coverage is obtained for any kind of substrate. Finally, the CA measurements indicate that the polar component of the surface free energy is directly related to both the amount and the orientation of the adsorbed amino acid molecules.

10:00am **BI+SS-WeM6 Surface-bound Liposomes for Biomedical Applications***, P. Vermette,* CSIRO, Australia*; E. Gagnon,* Universite Laval, Canada*; L. Meagher,* CSIRO, Australia*; D. Dunstan,* Melbourne University, Australia*; **H.J. Griesser**,* CSIRO, Australia*; C. Doillon,* Universite Laval, Canada

Injectable liposomes, in particular PEG-coated liposomes, are well known in the pharmaceutical industry for drug delivery. However, much of the drug never reaches the intended target site. We have developed methods for binding liposomes onto surfaces of biomedical devices for controlled local delivery of drugs adjacent to implanted biomedical devices. In this way we aim to reduce drug amounts and wastage, and control the local host response to the implant, a response which with most current biomaterials typically is dominated by fibrous tissue encapsulation. We have produced liposomes with encapsulated drugs and model substances, characterized them in terms of size and release performance, and bound them onto polymeric surfaces. PEGylated phospholipid liposomes were produced by extrusion through polycarbonate membranes of various pore sizes. The diameters of the liposomes were characterized by photon correlation spectroscopy. For binding liposomes, polymer surfaces were coated with streptavidin, which was used for affinity capture of biotinylated PEGylated liposomes. Streptavidin was covalently bound onto polymer surfaces via an amine plasma (glow discharge) polymer interlayer and a layer of polyacrylic acid, onto whose carboxylate groups the streptavidin was attached by carbodiimide chemistry. Detailed surface analyses were used to characterize and verify each step in the fabrication of the liposome coated surfaces. To test the in vivo efficacy of liposome coated biomaterials, an angiogenesis promoting drug was encapsulated and the liposomes attached. Both in vitro and in vivo there occurred markedly enhanced angiogenesis. Another way of using the same concept may be to implant streptavidin coated biomedical implants and then inject drug-loaded liposomes. Experiments are currently underway to investigate whether circulating biotinylated liposomes can thus be enriched at an implant surface by affinity capture with surface-immobilized streptavidin.

10:20am **BI+SS-WeM7 Thiol-Reactive Surfaces for the Specific Immobilization of Biomolecules***, **R.L. Cicero**, D. Martin, S. McManus-Munoz, C.E.J. Dentinger, P. Kernen, P. Wagner,* Zyomyx Inc.

We present multi-component self-assembled monolayers on Au(111) surfaces that extend thiol-reactive groups and chemical moieties known to resist non-specific adsorption of proteins. Particular attention will be paid to the structural characterization of these surfaces using X-ray photoelectron spectroscopy, reflection absorption infrared spectroscopy and ellipsometry. We also investigate the effect surface density of thiol-reactive groups presented at the solid-liquid interface has with respect to homogeneity, efficiency and specificity of immobilizing thiol-containing biomolecules to these surfaces. Several methods for detecting and quantifying biomolecule immobilization are used including surface plasmon resonance spectrometry, radiometry and fluorimetry.

10:40am **BI+SS-WeM8 Control and Detection of Surface Immobilized DNA Interactions Using Electrostatically Assisted Surface Plasmon Resonance***, **R.J. Heaton**, A.W. Peterson, L.K. Wolf,* Boston University*; R.M. Georgiadis,* Boston University, usa

Using Surface Plasmon Resonance (SPR) spectroscopy, we demonstrate that the formation of an immobilized DNA film on gold can be controlled by non-Faradaic electrostatic charging. Furthermore, electrostatic charging can be used to enhance interactions between the immobilized probe film and target oligonucleotides in solution. By simply adjusting the potential across the surface thiol-modified single stranded oligonucleotide films can be formed with good reproducibility in coverage. The application of an attractive potential can speed up and maximize the hybridization of complementary and mismatched oligonucleotides to the probe film. We demonstrate the efficacy of this technology with application to both single area and array-mode SPR.

11:00am **BI+SS-WeM9 Non-Uniform Mixing in Fluid Surfaces***, **J.S. Hovis**, S.G. Boxer,* Stanford University

Cell membranes are two-dimensional heterogeneous fluid surfaces comprised of lipids, proteins, and carbohydrates. Understanding their organization at the molecular level is of critical importance for understanding cellular function. One of the key features, of the cell membrane is it's fluidity, which precludes long range order. However, due to the heterogeneous nature of the system it is possible that non-uniform mixing occurs, resulting in the local enhancement of certain membrane components. We will present results from our studies designed to probe for one type of domain, termed 'lipid rafts', using model membranes. In particular, we use supported lipid bilayers that are partitioned; the partitioning enables us to spatially contain the membrane components. By applying an electric field in the plane of the bilayer we can rearrange the membrane components in the partitioned regions. Sphingolipids and cholesterol, the major components of lipid rafts are electrically neutral and will not reorganize in response to a field; however, GM@sub 1@, a minor component, will as it has a net negative charge. Using epi-fluorescence microscopy we monitored the resultant electric field induced reorganization of the membrane components. Our results indicate that the reorganization of the GM@sub 1@ induces a reorganization of the sphingolipids and cholesterol. However, this reorganization does not appear to be concerted, suggesting that the rafts are not long-lived structures. That is, there is an increased propensity for certain components to be in close proximity to one another, but due to the fluid nature of the lipid bilayer, individual components are not in close proximity for long. This work will hopefully provide additional insight into understanding how non-uniform mixing occurs in these fluid surfaces and what the functional consequences are.

11:20am **BI+SS-WeM10 Vesicle to Supported Bilayer Transformation Kinetics; Influence from Vesicle Size, Temperature and Surface Support***, **E. Reimhult**, K. Dimitrievski, V.P. Zhdanov, F. Höök, B. Kasemo,* Chalmers University of Technology, Sweden

Supported phospholipid bilayers (SPB) on solid surfaces are biologically functional components of high current interest, e.g., for biosensors, tissue engineering, and basic science (Sackman, Science 271:43 (1996)). We investigate how the kinetics of vesicle to bilayer transformation on SiO@sub 2@ depend on vesicle size using small Extruded Unilamellar Vesicles (EUV; diameter~30-200 nm) and Small sonicated Unilamellar Vesicles (SUV; diameter~25 nm)) and temperature (T~5 to 30°C).). The experimental results are complemented by computer modeling and MC simulations. Our results reveal weak but significant vesicle size-dependent kinetics. The rate and completeness of the vesicle-to-bilayer transformation is strongly dependent on temperature and the vesicle-to-bilayer formation on SiO@sub 2@ can under certain circumstances be completely inhibited at low temperatures. In addition, the vesicle-surface interaction was investigated for various surfaces, including oxidized Au, Pt and Ti, which all demonstrate adsorption of vesicles in an intact state independent of vesicle size and temperature. The obtained results extend our previous studies at constant vesicle size and temperature (Keller et al, Phys Rev B 61: (3) 2291 (2000)) and constitute a platform that will significantly improve the possibility to control the process on µmm-nm fabricated surfaces, from which more complex functional supported bio-membranes are constructed.

11:40am **BI+SS-WeM11 Functional Tethered Lipid Membranes on Gold***, **K. Bender**,* Stanford University

A solid supported, biomimetic lipid bilayer was formed on a gold substrate by adsorbing lipid vesicles on a self-assembled monolayer (SAM) consisting of thiol-lipopeptides mixed with thiol-peptides. The membrane was bound to the surface by the thiol-lipopeptides, the thiol-peptides being used to change the surface concentration of thiol-lipopeptide and hence control membrane fluidity. The lipid bilayer was formed by fusion of L-@alpha@-Phoshatidylcholine (eggPC) liposomes onto the mixed thiol-lipopeptide / thiol-peptide SAM. The free lipids replenish the tethered lipid layer and also form the second layer to complete the bilayer. A functionalized lipid bilayer was formed by incorporating H@super +@-ATP-synthase (extracted and purified from spinach chloroplastes) with the eggPC. This enzyme is a membrane integral protein that can synthesize or hydrolyze adenosine triphosphate (ATP) from or to adenosine diphosphate (ADP) and in doing so pumps H@super +@ through the bilayer. Impedance spectroscopy measurements demonstrated that the enzyme had not lost its biological functionality and was still active. The formation of the lipid bilayer was detected by using surface plasmon resonance spectroscopy (SPS). Finally Annexin V, a pore forming protein, was immobilised on a lipid bilayer by using Ca@super 2+@-ions to bind (by chelation) the negatively charged parts of the protein to the negatively charged lipids (1,2-Dimyristoyl-sn-Glycero-3-Phoshatidylserin) in the bilayer. Annexin V as a non-integral protein and its function as a passive ion transporter through the lipid bilayer was used for comparison of the active ion transporter H@super +@-ATP-synthase. The same techniques as described above were used to observe the formation and activity of this system.

Dielectrics
Room 130 - Session DI-WeM

Atomic Layer Deposition for Silicon Devices

Moderator: P.S. Ho, The University of Texas at Austin

8:20am **DI-WeM1 Growth of Tantalum Oxide Films by Chemical Vapor and Atomic Layer Deposition***, **S. Prasertchoung**, S.-Y. Yang, J.N. Kidder,* University of Maryland

The nucleation and growth of tantalum oxide thin films by chemical vapor and atomic layer deposition was studied. In the CVD process, the films were deposited using Ta(C@sub 2@H@sub 5@O)@sub 5@ and O@sub 2@ as precursors, where tantalum source was delivered to the process using direct liquid injection. Films with thickness of 1 to 50 nm were deposited on Si and Pt-coated Si substrates and characterized using ellipsometry, atomic force microscopy, X-ray diffraction, and electrical measurements. In the CVD process it was observed that the deposition rate was kinetically-limited at substrate temperatures up to 475 C with an activation energy of approximately 1 eV. At temperatures greater than 475 C the growth rate decreased significantly and film properties were poor with rough morphology. This behavior was characteristic of gas phase reaction effects, although similar behavior was observed even with sequential delivery of the oxygen and tantalum ethoxide, where reactions between the precursors were minimized. This effect may stem from reactions with by-products of the alkoxide decomposition, such as water and ethanol, which can have a large effect on the nucleation and growth. In this work we investigated the effect of water on the initial nucleation, the growth kinetics, and the film morphology for ultra thin films of tantalum oxide deposited in both chemical vapor deposition and atomic layer deposition processes where the precursors (Ta(C@sub 2@H@sub 5@O)@sub 5@, O@sub 2@, H@sub 2@O) were delivered under various sequences and conditions. @FootnoteText@ This work was supported by the NSF through the University of Maryland MRSEC(DMR 00-80008).

8:40am **DI-WeM2 Quantum Chemical Study of Zirconium Oxide Atomic Layer Deposition***, **Y. Widjaja**, C.B. Musgrave,* Stanford University

As gate oxide thickness in MOS device decreases, new high-@kappa@ materials are being investigated to substitute for silicon oxide. However, unlike silicon oxide, the oxide layers being investigated do not react readily on silicon surfaces. Here, we use density functional theory to examine the atomic layer deposition of zirconium oxide, one of the high-@kappa@ materials candidates, on the Si(100)-(2x1) surface. The reactants investigated in this study are ZrCl@sub 4@ and H@sub 2@O. The atomistic mechanisms of two different deposition cycles are investigated: 1) ZrCl@sub 4@ is first deposited on the clean Si(100)-(2x1) surface. Upon adsorption, ZrCl@sub 4@ is shown to dissociate into ZrCl@sub 3@(a) and Cl(a) with an activation barrier that is below the entry level. Water is deposited next and various surface reactions and configurations are investigated. We find that the most stable species consists of ZrCl@sub 3@(a) and OH(a) attached to the two silicon atoms of silicon dimers. Alternatively, 2) H@sub 2@O is first deposited on the Si(100)-(2x1) surface. As determined previously, we also find that H@sub 2@O dissociates into OH(a) and H(a) upon adsorption. Subsequent reactions with ZrCl@sub 4@ are then investigated. Upon investigation of the two different deposition cycles, the properties of the interfacial layer between silicon and zirconium oxide are then investigated. Subsequent half cycle reactions on the zirconia surface will also be presented.

9:00am **DI-WeM3 Effect on In-situ H@sub 2@ Plasma Treatment of ZrO@sub 2@ Gate Dielectric Deposited by Plasma Enhanced Atomic Layer Deposition Method***, J.H. Koo, **Y. Kim**, H. Jeon,* Hanyang University, Korea

As the metal oxide semiconductor device continues scale down, the high-k gate dielectrics become one of the solutions in providing increased capacitance and reduced leakage currents without significantly increasing the actual equivalent oxide thickness (EOT) of gate dielectrics. Among the high-k materials, ZrO@sub 2@ is considered as one of the alternatives to SiO@sub 2@ gate dielectric due to the relatively high dielectric constant (~25), low leakage current and its compatibility with the manufacturing of integrated circuits.@footnote 1@ Here, we focus on the in-situ H@sub 2@ plasma effect on ZrO@sub 2@ gate dielectric deposited by plasma enhanced atomic layer deposition (PEALD) method. ZrO@sub 2@ were deposited on p-type Si (100) substrates at 200-300°C using t-butoxide as Zr precursor and oxygen as reactant gas at the process pressure of about 1 Torr. Initial native oxide layer was removed by in-situ hydrogen plasma treatment before ZrO@sub 2@ deposition at the same processing temperature. Oxygen reactant gas was introduced both as in gas and plasma states. About 1000Å layer of Platinum (Pt) as gate electrodes were deposited by e-beam evaporator. The electrical properties of this MOS capacitor were measured after post metal annealing. The physical and chemical characteristics of ZrO@sub 2@ film were analyzed by cross-sectional transmission electron microscope, atomic force microscope, Auger electron spectroscopy, X-ray photoelectron spectroscopy and Rutherford backscattering spectroscopy. The results of electrical properties and reliability characteristics including EOT, hysteresis, leakage current and capacitance were measured by I-V and C-V. This paper presents the plasma effect on ZrO@sub 2@ films deposited by PEALD method and its potential applications for gate dielectric in ultra large-scale integrated circuit devices. @FootnoteText@ @footnote 1@W. Qi, R. Nieh, B. H. Lee, L. Kang, Y. Jeon and J. C. Lee, Appl. Phys. Lett., 77, 3269-3271 (2000).

9:20am **DI-WeM4 Nucleation and Growth Chemistry during Tungsten Atomic Layer Deposition on Oxide Surfaces***, **R.K. Grubbs**,* University of Colorado, Boulder, U.S.A

The nucleation and growth chemistry during tungsten (W) atomic layer deposition (ALD) on SiO@sub 2@ and Al@sub 2@O@sub 3@ surfaces were studied using Auger electron spectroscopy and quadrupole mass spectrometry. W ALD was performed using sequential exposures of WF@sub 6@ and Si@sub 2@H@sub 6@. Differences in the nucleation process and the film growth mode were observed for the two oxide substrates. The nucleation of W ALD on SiO@sub 2@ required 8-9 WF@sub 6@/Si@sub 2@H@sub 6@ reaction cycles. A much shorter nucleation period was observed on Al@sub 2@O@sub 3@. W ALD on SiO@sub 2@ followed a Frank-Van der Merwe, layer-by-layer, growth mode while W ALD on Al@sub 2@O@sub 3@ occurred with a Volmer-Weber growth mode. These results indicate that the identity of the underlying substrate has an affect on the nucleation and growth of W ALD films. The growth chemistry of W ALD was studied using quadrupole mass spectrometry. The reaction products from each sequential reaction were identified and correlated with the Auger results. The reaction products suggest the stoichiometry of the surface reactions during tungsten atomic layer deposition.

9:40am **DI-WeM5 Atomic Layer Deposition of Al@sub 2@O@sub 3@/ZnO Nanolaminates and Alloys: Fabrication and Properties***, **J.W. Elam**, M.D. Groner, Z.A. Sechrist, S.M. George,* University of Colorado

Atomic layer deposition (ALD) of Al@sub 2@O@sub 3@ and ZnO films can be accomplished using sequential exposures to Al(CH@sub 3@)@sub 3@/H@sub 2@O and Zn(CH@sub 2@CH@sub 3@)@sub 2@/H@sub 2@O, respectively. ALD Al@sub 2@O@sub 3@ is smooth, amorphous and insulating. ALD ZnO is rough, crystalline and conducting. Composite mixtures of Al@sub 2@O@sub 3@ and ZnO may have unique and interesting properties. Al@sub 2@O@sub 3@/ZnO nanolaminates and alloys were deposited by ALD in a viscous flow reactor. The Al@sub 2@O@sub 3@/ZnO composite film growth was monitored using an in situ quartz crystal microbalance. A series of Al@sub 2@O@sub 3@/ZnO nanolaminates was prepared where the total thickness of Al@sub 2@O@sub 3@ and ZnO was kept constant while varying the number of individual Al@sub 2@O@sub 3@/ZnO bilayers. Atomic force microscopy was used to measure the root mean squared (RMS) surface roughness of the Al@sub 2@O@sub 3@/ZnO nanolaminate films. The RMS roughness of the nanolaminate films decreased dramatically versus the number of Al@sub 2@O@sub 3@/ZnO bilayers. A series of Al@sub 2@O@sub 3@/ZnO alloy films was also grown using ALD by varying the relative number of Al(CH@sub 3@)@sub 3@/H@sub 2@O and Zn(CH@sub 2@CH@sub 3@)@sub 2@/H@sub 2@O sequential exposures. Four-point probe and mercury probe measurements were performed to determine the resistivity of the Al@sub 2@O@sub 3@/ZnO alloys. The resistivity of the Al@sub 2@O@sub 3@/ZnO alloy films decreased with small Al@sub 2@O@sub 3@ percentage and then increased greatly with increasing Al@sub 2@O@sub 3@ percentage. These studies of the fabrication and properties of ALD composite films will serve as a model for the future development of ALD aluminates and silicates.

10:20am **DI-WeM7 Radical Enhanced Atomic Layer Deposition of TiN Diffusion Barriers*, F. Greer,*** *D. Fraser, J.W. Coburn, D.B. Graves,* University of California, Berkeley

Atomic Layer Deposition (ALD) has been proposed as one way to deposit highly conformal thin films for copper diffusion barriers due to the self-limiting, layer-by-layer growth that can be achieved with this technology. One problem with thermally activated ALD is that the deposition temperatures that are required to achieve reasonable growth rates and good quality films with low impurity concentrations can be relatively high. This may make the integration of these barrier films with temperature-sensitive films, such as organic low-k films, impossible. One potential alternative to thermal ALD is to use more reactive species such as radicals to catalyze film deposition at lower substrate temperatures. In this work, TiN films are deposited using Radical Enhanced Atomic Layer Deposition (RE-ALD) using separate, alternating pulses of TiCl@sub 4@ and various combinations of hydrogen and/or nitrogen radicals with or without additional pulses of NH@sub 3@. By directing independent beams of each of these species at a given surface (in this case, silicon dioxide coated on Quartz Crystal Microbalances), kinetic parameters of interest such as the sticking and reaction probabilities of these species have been measured as a function of surface temperature, and will be used to predict the conformality of films deposited using RE-ALD in features of arbitrary aspect ratio. Ex-situ XPS analysis of the deposited films will be presented, paying particular attention to the low residual chlorine content that can be achieved with sufficient hydrogen radical exposure (~0.3%) at deposition temperatures as low as 100°C. In-vacuo Auger Electron Spectroscopy film composition measurements will be presented from different stages during the deposition process. Various measurements of the film quality will also be presented including the dependence of the films' resistivity and crystallinity on deposition conditions.

10:40am **DI-WeM8 Characteristics of Tungsten Nitride Atomic Layer Deposition*, H.S. Sim,*** Korea Institute of Science and Technology*; Y.T. Kim,* Korea Institute of Science and Technology, Korea*; H. Jeon,* Hanyang University, Korea

Atomic layer deposition method for binary or ternary metal nitride film such as TiN, W-N, TaN, and TiSiN has been proposed to get a nano-scale diffusion barrier thin film. In this work, we have deposited W-N atomic layer with multiple cycles of introducing WF@sub 6@, N@sub 2@, NH@sub 3@, and N@sub 2@ gases in order. A cycle time was varied from 1 - 5 sec for an atomic layer. Deposition rate per cycle, crystal structure, and atomic lattice image for interface of W-N and Si were determined with high resolution transmission electron microscopy (HR-TEM). We have investigated atomic deposition windows at temperatures between 250 - 450 °C. As a result, deposition rate per cycle was nearly the same and the resistivity of as deposited W-N was about 100 ~ 300 µ@OHM@-cm. The diffusion barrier performance of both as-deposited and post-annealed W-N films at temperatures between 500 and 700 °C were investigated in the view points of Cu diffusion mechanisms through surface and grain boundary. As a nano scale diffusion barrier for Cu interconnect, we have investigated correlations between Cu diffusion and texture, composition change and crystalline structures of W-N atomic layer during post-annealing with medium energy ion spectrometry (MEIS) as well as HR-TEM.

11:00am **DI-WeM9 Deposition of Ultra Thin Films by Atomic layer Deposition (ALD)*, M.A. Leskela,*** University of Helsinki, Finland **INVITED**

In ALD the precursors are pulsed to the substrate alternately one at the time and between the reactant pulses the reactor is purged with an inert gas. With a proper adjustment of the conditions the process can proceed via saturative steps. The precursors chemisorb on the surface or react with the surface groups and form a tightly bound monolayer. Under such conditions the growth is stable and the thickness increase is constant in each deposition cycle. The layer-by-layer principle facilitates the growth of ultra thin films with accurate thickness and conformality on large areas. These advantages of the ALD method are just those required in microelectronics for the manufacturing of future generation integrated circuits. In microelectronics ALD has been studied for deposition of oxide films for dielectrics, nitride films for diffusion barriers for metallizations, and metal films. Examples of those processes will be given. The key issue in a successful ALD process is the precursor chemistry. The development of new precursors is a challenge for the further progress of ALD. ALD can also be used to modify interfaces of thin film structures and surfaces of powder samples. Examples from the use of ALD in preparation of heterogeneous catalysts will be highlighted.

Electronics
Room 111 - Session EL+MI-WeM

Spintronics III: Ferromagnetic Semiconductors

Moderator: C.J. Palmstrom, University of Minnesota

8:20am **EL+MI-WeM1 Tailoring Spin Ordering in Magnetic Semiconductors*, T. Dietl,*** Polish Academy of Sciences, Poland, Warszawa **INVITED**

Recent advances@footnote 1@ in the field of carrier-controlled ferromagnetism in tetrahedrally coordinated diluted magnetic semiconductors and their nanostructures will be reviewed with a focus on the phenomena important for prospective spintronic devices. Experimental results for III-V materials, where the Mn atoms introduce both spins and holes, will be compared to the case of II-VI compounds, in which the Curie temperatures T@sub C@ above 1 K have been observed for the uniformly and modulation-doped p-type structures but not in the case of n-type films. The experiments demonstrating the tunability of T@sub C@ by electrostatic gates as well as by light will be presented. The tailoring of domain structures and magnetic anisotropy by strain engineering and confinement will be discussed emphasizing the role of the spin-orbit coupling in the valence band. The question of designing modulated magnetic structures in low dimensional semiconductor systems will be addressed. Recent progress in search for semiconductors with T@sub C@ above room temperature and hopes associated with materials containing magnetic ions other than Mn will be presented. @FootnoteText@ @footnote 1@ T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, Science 287, 1019 (2000); H. Ohno et al., Nature 408, 944 (2000); P. Kossaki et al., Physica E 6, 709 (2000); D. Ferrand et al., Phys. Rev. B 63, 085201 (2001); T. Dietl, H. Ohno, and F. Matsukura, Phys. Rev. B 63, 195205 (2001).

9:00am **EL+MI-WeM3 Dilute Magnetic Semiconductors Based Upon GaP*, M.E. Overberg,*** *C.R. Abernathy, S.J. Pearton, N. Theodoropoulou, A.F. Hebard,* University of Florida*; S.N.G. Chu,* Agere Systems*; R.G. Wilson,* Consultant

Dilute magnetic semiconductors (DMS), where a semiconductor host material is heavily doped with magnetic ions, could potentially be used in a variety of interesting applications and devices where the spin degree of freedom of the electron is exploited, such as quantum-based computation, electro-optic switches and modulators, to name a few. Recent theoretical calculations based upon a 5% concentration of Mn have predicted a Curie temperature for (Ga,Mn)P of roughly 100 K.@footnote 1@ The challenge is to incorporate such a large amount of magnetic ions while still maintaining the integrity of the host semiconductor. In this paper, we will report on the growth of (Ga,Mn)P:C thin films by gas source molecular beam epitaxy (GSMBE) utilizing phosphine as the group V source, and co-doped with C via a CBr@sub 4@ source for enhanced p-type doping. Results of the epitaxially grown films will be compared to (Ga,Mn)P films produced via direct implantation of Mn into GaP:C, particularly in regard to the formation of alternate phases and how this correlates with the observed magnetic behavior. X-ray diffraction (XRD) of the epitaxial films indicates the presence of the orthorhombic MnP phase in layers grown at a temperature of 600°C, and in addition the hexagonal Mn@sub 5.64@P@sub 3@ phase in films grown at a temperature of 400°C. At lower temperatures, only the Mn@sub 5.64@P@sub 3@ phase exists. The use of superlattices appears to help suppress the second phase formation, particularly in the low temperature regime. Analysis of the GaMnP:C by SQUID magnetometry suggests the presence of a ferromagnetic phase with a T@sub C@ above 50 K. This behavior is most likely due to the presence of ferromagnetic MnP. In an effort to increase the T@sub C@ above that which is possible when using Mn, the properties of Ni implanted GaP:C will also be presented. @FootnoteText@ @footnote 1@ T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, Science, 287, p. 1019 (2000).

9:20am **EL+MI-WeM4 Epitaxial Growth of a Group IV Ferromagnetic Semiconductor: Mn@sub x@Ge@sub 1-x@***, **A.T. Hanbicki**, Y.D. Park, A. Wilson, G. Spanos, B.T. Jonker,* Naval Research Laboratory

Ferromagnetic semiconductors promise to provide spin-dependent functionality to the well-established technology of semiconductor device heterostructures. While much effort has focused on the III-Mn-V materials such as GaMnAs, where hole density is believed to play a critical role, the origins of ferromagnetic (FM) order remain elusive. This is due in part to complications arising from use of compound semiconductor hosts. Mean field calculations predict that FM order should be stabilized in many other semiconductor materials, if certain Mn concentrations and hole densities can be realized.@footnote 1@ We have chosen one of the simplest semiconductor hosts, Ge, in which to investigate and better understand such effects. We report here the epitaxial growth of the first Group IV ferromagnetic semiconductor, Mn@sub x@Ge@sub 1-x@, and describe the structural, magnetic, and magneto-transport properties. Single crystal films were grown for x < 0.1 on GaAs(001) and Ge(001) substrates by MBE at low substrate temperatures from elemental sources. RHEED and x-ray diffraction confirm crystallinity and orientation. Samples exhibit hysteretic M vs H loops with significant remanence, and coercivities of several hundred Gauss. Curie temperatures range from 30 to 120 K with increasing Mn concentration, as determined from SQUID magnetometry. Films exhibit a non-metallic temperature dependent resistivity, as well as a pronounced extraordinary Hall effect. They are strongly p-type with hole densities of 10@super 19@ - 10@super 20@ cm@super -3@. Gated structures confirm that the hole density can be varied. Results will be presented on efforts to toggle ferromagnetism by application of a gate voltage at temperatures significantly higher than recently reported for InM nAs.@footnote 2@ This work was supported by the DARPA SpinS program and ONR. @FootnoteText@ @footnote 1@ T. Dietl, et al., Science 287, 1019 (2000). @footnote 2@ H. Ohno et al, Nature 408, 944 (2000).

9:40am **EL+MI-WeM5 Metalorganic Chemical Vapor Deposition of ZnO-based Diluted Magnetic Semiconductors***, **A.C. Tuan**[1],* University of Washington*; D. McCready, S. Thevuthasan, J.W. Rogers, Jr., S.A. Chambers,* Pacific Northwest National Laboratory

One of the most attractive means of adding the electron-spin degree of freedom to electronic and photonic devices is by spin injection and transport in semiconducting structures involving ferromagnetic metals or ferromagnetic dilute magnetic semiconductors (DMSs), as spin injectors. A great deal of work has been done in this area and thus far, DMSs have proven to be more efficient spin sources than ferromagnetic metals. This is because the conductivities of DMSs are better matched to those of the channel material. However, because of the very low ferromagnetic ordering temperature of current DMSs, efficient spin injection is only observed at cryogenic temperatures. A recent calculation predicts that heavily nitrogen-doped Mn@sub X@Zn@sub 1-X@O will exhibit a Curie temperature of ~320K,@footnote 1@ and serves as partial motivation for this work. We have grown Mn@sub X@Zn@sub 1-X@O films by metalorganic chemical vapor deposition (MOCVD), using a direct liquid injection system and @beta@-diketonate metal sources. Rutherford backscattering spectrometry (RBS) and X-ray photoelectron spectroscopy (XPS) show that compositions ranging from pure ZnO to ~Mn@sub 0.30@Zn@sub 0.70@O are achievable on Al@sub 2@O@sub 3@(0001) substrates, without carbon contamination. X-ray diffraction (XRD) was used to confirm that there was no phase segregation. XRD also indicated that all films grown below 500 °C had a preferred (0001) orientation, while epitaxy of ZnO was possible at 575 °C on both Al@sub 2@O@sub 3@ (0001) and ZnO(0001). Preliminary attempts at nitrogen incorporation show that NH@sub 3@ is a promising nitrogen source. @FootnoteText@ @footnote 1@T. Dietl, H. Ohno, F. Matsukura et al., "Zener model description of ferromagnetism in zinc-blende magnetic semiconductors," Science 287, 1019-22 (2000).

10:00am **EL+MI-WeM6 Heterostructures of Mn/GaN and MnGa/GaN Grown by ECR-Plasma Assisted MBE***, Y. Cui, **L. Li**,* University of Wisconsin

Ferromagnetic semiconductor GaMnN is very promising for developing spintronic devices.@footnote 1@ To investigate the mechanism of Mn incorporation in GaN, we have grown digital heterostructures by alternately depositing GaN (10 to 50 monolayers) and monolayer of either Mn or MnGa using ECR plasma assisted molecular beam epitaxy. The heterostructures are grown on 6H-SiC(0001) substrate with plasma power of 30 W at 550 °C. Adsorption and desorption of the Mn and MnGa on the non-growing surface, surface reactions and reconstruction are monitored by reflection high-energy electron diffraction (RHEED) and in situ scanning tunneling microscopy (STM). All the surfaces immediately following MBE are composed of spiral hillocks, with the edges of the spirals form bilayer steps. On the terraces, a gallium rich (1x1) structure is observed with a lattice spacing of 3.2 Å. At temperatures between 500 and 550 °C, deposition of approximately 1 ML of Mn on this surface results in a domain superstructure with a periodicity of ~ 32 Å. Within the domains the surface atoms are in (@sr@3x@sr@3) geometry. By closely monitoring the surface reconstruction present during MBE, heterostructures with high crystalline quality are grown, as confirmed by high-resolution x-ray diffraction. These results and their implications for Mn doping of GaN will be presented at the meeting. This research is supported by NSF DMR-0094105. @FootnoteText@@footnote 1@T. Dietl et al., Science 287, 1019 (2000).

10:20am **EL+MI-WeM7 Epitaxial Growth of GaMnN***, **G.T. Thaler**, M.E. Overberg, C.R. Abernathy, S.J. Pearton, N. Theodoropoulou, A.F. Hebard,* University of Florida

Dilute magnetic semiconductors (DMS) offer the use of the spin degree of freedom of the electron in addition to its charge in device applications. Recent theoretical calculations have predicted a Curie temperature for GaMnN of roughly 400 K.@footnote 1@ In this talk we will discuss the feasibility of growing GaMnN via gas-source molecular beam epitaxy. Mn levels up to 47% as determined by Auger electron spectroscopy (AES) have been obtained in GaMnN. X-ray diffraction (XRD) shows no evidence of second phase formation in films with Mn concentrations less than 9%. Addition of Mn to the GaN changes the conductivity from highly conductive n-type to highly resistive, suggesting that at least some of the Mn behaves as a deep acceptor. Nominally semi-insulating GaMnN with a Mn concentration of ~5% shows paramagnetic behavior with a saturation moment per Mn of 3.9 Bohr magnetons, suggesting that much of the Mn is substitutional. Increasing the growth temperature increases the electron concentration due to enhanced incorporation of nitrogen vacancies. The increased carrier concentration produces what appears to be a ferromagnetic material, but with a low Curie temperature of ~100K. Similar studies on p-GaMnN will be discussed in this talk as will the effect of adding Al to the GaMnN. @FootnoteText@ @footnote 1@ T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, Science, 287, p. 1019 (2000).

10:40am **EL+MI-WeM8 The Investigation of MnScN Grown by Molecular Beam Epitaxy***, **H.A.H. Al-Brithen**, H. Yang, A.R. Smith,* Ohio University

Nitride semiconductors are well known as important materials due to their unique electronic and optical properties. If it is possible to incorporate magnetic species (i.e. Mn or Fe) into nitrides, these may also be used as magnetic semiconductors for spintronics. Scandium nitride, shown to be a semiconductor, has been studied lately for its potential electronic applications.@footnote 1@ Since both MnN and ScN are known to exist with octohedral bonding,@footnote 2@ it seems likely that Mn may be soluble in ScN. Thus, we have undertaken a study of the growth of MnScN by molecular beam epitaxy. Mn@sub x@Sc@sub 1-x@N growth is initiated on a buffer of ScN grown on MgO(001). Growth has been performed for samples at substrate temperature between 350°C and 650°C with Mn/Sc intended flux ratios of 10 and 20%. For all samples, XRD reveals a clear alloy peak which is distinguishable from the ScN and MgO peaks. From the comparison of the alloy peak position with that of ScN and the expected peak position of MnN (based on separate studies of this binary compound@footnote 3@), the values of x are estimated and found to be in good agreement with the Mn/Sc flux ratios. RHEED patterns shows smooth growth on the ScN buffer at the initial stage. The evolution of the RHEED pattern depends on the substrate temperature and the Mn flux. For Mn/Sc ratio of 10%, the RHEED pattern show only a single phase with smooth growth; but for Mn/Sc ratio of 20%, some weak ring structures are observed after extended growth time, indicating a possible limit to the solubility of Mn in ScN. Studies of the magnetic properties of the MnScN alloy are underway. Work is supported by NSF. @FootnoteText@ @footnote 1@ H. A. Al-Brithen and A. R. Smith, Appl. Phys. Lett., 77, 2485 (2000); A.R. Smith et al., to be published. @footnote 2@ Suzuki et al., J. Alloys and Compounds 306, 66 (2000) @footnote 3@ H. Yang et al., Appl. Phys. Lett. 78, 3860 (2001).

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[1] **Falicov Student Award Finalist**

11:00am **EL+MI-WeM9 MBE Growth and Properties of Co-doped TiO@sub 2@ Anatase***, **S.A. Chambers**, S. Thevuthasan, D. McCready,* Pacific Northwest National Laboratory*; R.F.C. Farrow, R.F. Marks, L. Folks,* IBM Almaden Research Center*; N. Ruzycki, D.L. Ederer, U. Diebold,* Tulane University

The realization of fully functional spintronics requires semiconductors that are magnetic at ambient temperature. In a recent publication@footnote 1@, Co-doped anatase TiO@sub 2@ (Co@sub x@Ti@sub 1-x@O@sub 2@) epitaxial films grown on SrTiO@sub 3@(001) and LaAlO@sub 3@(001) by laser ablation were shown to exhibit weak ferromagnetism at room temperature for x up to 0.08. We have grown Co@sub x@Ti@sub 1-x@O@sub 2@ by oxygen-plasma-assisted molecular beam epitaxy on SrTiO@sub 3@(001) and SrAlLaO@sub 4@(001) substrates, for which the lattice mismatches are -3.1% and -0.8%, respectively. Preliminary results have confirmed that this material can be ferromagnetic at room temperature. Kerr effect measurements on some samples show larger remanence (>40%) than that seen in fig. 3 of ref. 1. In all cases, reflection high-energy electron diffraction measured during growth reveals that the film surface becomes progressively more disordered with increasing thickness, with secondary phases and/or complete disordering occurring after several tens of nm. X-ray diffraction reveals the presence of rutile in some cases. X-ray photoemission and x-ray absorption spectroscopy carried out at the LBNL Advanced Light Source reveal that Co is extremely mobile in the anatase lattice, and in most cases has a tendency to concentrate in the near-surface region. In addition, these spectroscopies reveal that Co in the ferromagnetic films is nearly 100% Co(II), whereas a mix of Co(II) and Co(III) is found in nonmagnetic films. Hall effect and TEM measurements are being carried out at the time of abstract preparation, and will be discussed at the conference. These preliminary results reveal that the single largest obstacle to reproducibility is the extremely facile diffusion of Co in the anatase lattice. @FootnoteText@ @footnote 1@Y. Matsumoto, M. Murakami, T. Shono, T. Hasegawa, T. Fukumura, M. Kawasaki, P, Ahmet, T. Chikyow, S.-Y. Koshihara, and H. Koinuma, Science, 291, 854 (2001).

11:20am **EL+MI-WeM10 Epitaxial Growth of an n-Type Ferromagnetic Semiconductor: CdCr@sub 2@Se@sub 4@@footnote *@***, **Y.D. Park**, A.T. Hanbicki,* Naval Research Laboratory*; J.E. Mattson,* Naval Research Laboratory, US*; B.T. Jonker,* Naval Research Laboratory

Ferromagnetic semiconductors (FMSs) provide unprecedented opportunity to tune and optimize spin-dependent behavior in semiconductor device heterostructures. Most efforts have focused on III-Mn-V materials such as GaMnAs, which are p-type only.@footnote 1@ Since efficient spin injection and very long spin scattering lengths have been confirmed for electrons rather than holes in semiconductors such as GaAs,@footnote 2-4@ one would like to realize FMS materials which are both n-type and can be epitaxially grown on a readily available device-quality substrate. We report here the epitaxial growth of FMS CdCr@sub 2@Se@sub 4@(001) films on both GaAs and GaP(001) substrates, and describe the structural, magnetic and electronic properties. The samples were grown by molecular beam epitaxy from elemental K-cell sources, and exhibit a 1x1 RHEED pattern during growth. The film structure, orientation and composition were determined by post-growth x-ray diffraction and fluorescence measurements. SQUID magnetometry data confirm ferromagnetic order with a Curie temperature of 130 K, as in the bulk material, and hysteretic behavior with significant remanence. The easy axis is in-plane with a coercive field of ~125 Oe. Temperature dependent transport data show that the films are semiconducting in character, and lightly n-type as grown. We further describe efforts at controlled doping and electrical spin injection from CdCr@sub 2@Se@sub 4@ contacts into GaAs-based LED heterostructures. @FootnoteText@ @footnote *@ This work was supported by the DARPA SpinS program and ONR. @footnote 1@ Ohno, Science 281, 951 (1998). @footnote 2@ Fiederling et al, Nature 402, 787 (1999). @footnote 3@ Jonker et al, PRB 62, 8180 (2000); Park el al, APL 77, 3989 (2000). @footnote 4@ Oestreich et al, APL 74, 1251 (1999).

11:40am **EL+MI-WeM11 Characterization of High Dose Mn, Fe and Ni Implantation into p-GaN***, **S.J. Pearton**, N. Theodoropoulou, A.F. Hebard,* University of Florida*; S.N.G. Chu,* Bell Laboratories, Lucent Technologies*; M.E. Overberg, C.R. Abernathy,* University of Florida*; R.G. Wilson,* Consultant*; J.M. Zavada,* U. S. Army European Research Office, UK

High concentrations (3-5at.%) of Mn, Fe and Ni were incorporated into p-GaN by direct implantation at elevated substrate temperature (350°C). Subsequent annealing at 700°C produced apparent ferromagnetic behavior below ~175 K for the 3at.% Fe sample and ~100 K for the 5at.% Fe sample. Selected area diffraction patterns did not reveal the presence of any other phases in the Fe-implanted region. For Mn-implantation, ferromagnetic contributions to the magnetization were observed below 250K in 3at.% samples. In this material, platelets consistent with the formation of GaMnN were observed by TEM. The direct implantation process appears promising for examining the properties of magnetic semiconductors with application to magnetotransport and magneto-optical devices.

Electronics
Room 124 - Session EL-WeM
Si Surface Dynamics and Reactions

Moderator: J.E. Rowe, Army Research Office

8:20am **EL-WeM1 Step Motion and Morphology on Si(111)***, **M.S. Altman**,* Hong Kong University of Science and Technology, Hong Kong **INVITED**

Surface steps are of interest for their role as templates for growth. Step morphology determined by thermodynamics can be influenced through step motion kinetics. Low energy electron microscopy observations of step flow, island nucleation and growth, and spiral growth at screw dislocations are the basis for studying step motion kinetics and the influence of surfactants upon growth. Sb and In surfactants are found to have notable and opposite influence on step kinetics. These results demonstrate that surfactants can be used to controlkinetically driven morphological instabilities, i.e., bunching and meandering, in step flow motion, and support the view that surfactants function at least partially through step passivation. However, surface phase separation is also observed as a consequence of surfactant incorporation during growth, which leads to a distinct step flow instability. Self-organized periodic step bunching patterns on vicinal surfaces will also be discussed.

9:00am **EL-WeM3 Step Fluctuations on a Chemically Heterogeneous Surface: Al/Si(111)-(@sr@3x@sr@3)@footnote 1@***, **I. Lyubinetsky**, D.B. Dougherty, E.D. Williams,* University of Maryland at College Park

Analysis of equilibrium step fluctuations has been extended for an adsorbate-induced reconstruction. The lateral and temporal correlations of single-height step fluctuations has been studied with variable temperature STM at 550-750° C on a vicinal Si(111) surface, miscut by 0.5° in the [2,-1,-1] direction, after formation of the Al-induced (@sr@3x@sr@3) surface phase. From direct measurement of the spatial step-correlation function, the step diffusivity, b@super 2@/a, is found to exponentially increase from 0.7 Å at 550°C to 1.19 Å at 750°C. The effective kink creation energy of 0.14 eV then has been extracted from corresponding Arrhenius plot. Results of analysis of lateral step correlations at elevated temperatures will also be compared with results obtained in traditional way by quenching surface down to the room temperature. The temporal correlation functions in this temperature region are shown to scale as t@super 1/2@, consistent with either step-edge attachment or terrace-crossing diffusion as a rate limiting process. The prefactor of the temporal correlation function also varies exponentially with temperature yielding an effective activation energy of 2.5 eV for the rate-limiting step in surface mass transport. Using both lateral and temporal correlation functions, the kinetic parameters governing mass transport have been extracted for different temperatures, and atomistic models for the step fluctuations will be discussed. @FootnoteText@ @footnote 1@ Work supported by the UMD-NSF-MRSEC.

9:20am **EL-WeM4 Atomic and Electronic Structure of Si Layers on CaF@sub 2@/Si(111)***, **A.A. Bostwick**, J.A. Adams,* University of Washington*; E. Rotenberg,* Advanced Light Source, Berkeley*; M.A. Olmstead,* University of Washington

Many forms of nanocrystalline silicon have been observed to luminesce at room temperature under photon or electron excitation. However, the relative importance of electron confinement and interface compounds is still an open question for many of these materials. Our group recently developed a means to fabricate ultrathin, crystalline, arsenic-terminated silicon quantum wells on calcium fluoride using electron irradiation in the presence of an arsenic surfactant flux.@footnote 1@ With no intrinsic oxygen and a well-defined surface and interface structure, these films make excellent candidates for probing the properties of oxygen-free silicon nanostructures. We have studied such films with angle-resolved valence band and core-level photoemission spectroscopy and diffraction and near-edge xray absorption spectroscopy. Our initial studies show no surface states in the bulk Si energy gap and a flat, weakly dispersing density of valence states. We also discuss growth mechanisms for these films, which are sensitive to the irradiation and arsenic exposure conditions.

@FootnoteText@ @footnote 1@ B. R. Schroeder, S. Meng and M. A. Olmstead, Appl. Phys. Lett. 77, 1289 (2000).

9:40am **EL-WeM5 Surface Mass Transport and Island Nucleation during Growth of Ge on Laser Textured Si(001)***, T. Schwarz-Selinger,* Max Planck Institut für Plasmaphysik, Germany*; **D.G. Cahill,*** University of Illinois, Urbana

Shape transitions and coarsening of coherent three-dimensional islands in Stranski-Kranstanow crystal growth have been extensively studied but quantitative descriptions of island nucleation kinetics are hindered by incomplete understanding of surface mass transport on the wetting layer. To gain new insights on wetting layer mass transport, we manipulate the spatial distribution of island nucleation by modifying the substrate morphology with laser texturing: fluid flow in the melt zone created by tightly-focused nsec pulses from a frequency doubled Nd:YAG produces shallow, micron-sized dimples on the Si substrate. We then use gas-source molecular beam epitaxy to deposit Ge and, finally, measure the distribution of three-dimensional Ge islands surrounding the laser dimples by atomic force microscopy. As expected, island nucleation starts at the vicinal surfaces near the rim of the dimple. These initial islands create a denuded zone of suppressed island nucleation on the flat regions of the substrate surrounding the dimple. Nucleation theory predicts that the extent of the denuded zone L should be comparable to the the island-island separation d but, in the limit of slow growth rates, we observe L/d>20. By comparing the denuded zone lengths produced by different growth rates (varied by a factor of 100) and substrate temperatures (500-600°C), we extract an activation energy for surface mass transport.

10:00am **EL-WeM6 Non-thermal SiO@sub 2@ Film Growth on Si(100) using Laser-generated O(@super 1@D) and O(@super 3@P)***, **T.C. Coulter,** A.C. Tuan,* University of Washington*; W.P. Hess, J.W. Rogers, Jr,* Pacific Northwest National Laboratory*; Y. Ono,* Sharp Labs of America

Thermal oxidation of silicon by O@sub 2@ or H@sub 2@O at high temperature (usually 800-1000°C) is currently used to achieve device-quality films for microelectronic applications. These high temperatures can degrade other device characteristics. As device dimensions shrink, it becomes even more important to keep processing temperatures low. Thus, many alternative low-temperature oxidation methods have been explored. A successful low-temperature method must produce thin silicon oxide layers with good uniformity, abrupt interfaces, and device-quality electrical characteristics. In order to develop the best low temperature deposition strategy, it is necessary to understand the details of the oxidation mechanism. High-temperature thermal oxidation studies suggest that atomic oxygen, and not molecular O@sub 2@, may be the oxidizing species diffusing through the oxide to react at the silicon interface. Low temperature plasma oxidation proceeds faster than thermal oxidation, which is often attributed to the presence of charged and neutral atomic species. Recent studies using a modified plasma for SiO@sub 2@ growth suggest that excited oxygen atoms in the @super 1@D state may play an important role in oxidation.@footnote 1@ To elucidate the roles of excited and ground state neutral oxygen atoms in silicon oxidation, we have used photolytically generated ground state O(@super 3@P) and excited state O(@super 1@D) atoms to oxidize Si(100) at low temperature. In contrast to plasma oxidation, where many oxygen species of differing energy and charge are present, we can study the contributions of O(@super 3@P) and O(@super 1@D) individually, and compare their kinetics and oxidation mechanism. The growth rate and oxidation kinetics were studied with in-situ ellipsometry, and oxide stoichiometry and interface quality were determined with XPS. @FootnoteText@ @footnote 1@M. Hirayama, K. Sekine, Y. Saito, and T. Ohmi. IEEE Transactions on Electron Devices. 47(7), 1370 (2000).

10:20am **EL-WeM7 On the Use of Angle-resolved XPS for Resolving Composition Structure of Ultrathin Inhomogeneous Oxide Layers***, **T. Conard**, H. De Witte, W. Vandervorst, J. Petry,* IMEC, Belgium*; R. White, K.S. Robinson,* Thermo VGScientific, UK

With the downscaling of electronic, the industry faces a large number of challenges. Among those, layers with an EOT lower than 1nm have to be engineered for the gate oxide. The materials considered can be silicon oxynitride, ZrO@sub 2@, Al@sub 2@O@sub 3@ as a single layer or as multistack. One common characteristic of all these films is there very limited thickness (a few nm at most) and the inhomogeneous distribution of elements throughout the stack. These films challenge thus most of the analysis techniques used for determining the layer structure and composition such as SIMS. For very thin layers, XPS is a possible alternative to sputtering techniques as it allows a non-destructive analysis through the whole film. The development of angle resolved XPS instruments with the ability to acquire spectra simultaneously over multiple angles should also give the possibility to retrieve the layer composition as a function of depth. This work concentrates on the interpretation of such ARXPS data and its application as an alternative and complementary technique to SIMS profiling. Particular in our experiments is the simultaneous collection of up to 16 emission angles (using a Thermo VG Scientific ThetaProbe) which provides unparalleled capabilities to reconstruct non-homogenous depth profiles in very thin layers. We will present results showing that small differences in the nitrogen distribution (near surface, in film, interfacial) inside thin (~3.5 nm) SiON layers can be determined using simultaneous ARXPS. In addition, the technique can also be used to understand the strong modification observed in the profiling of ZrO@sub 2@/SiO@sub 2@/Si stacks using Ar+ ions at energies between 500 eV and 3keV. The depth profiles reconstructed from the ARXPS provide information on the redistribution of Zr and O in the ion bombarded film allowing to interpret these modifications in terms of oxygen preferential sputtering and sputtering induced oxygen diffusion in the ZrO@sub 2@ layer.

11:00am **EL-WeM9 Silicon-Oxide Formation on Gold***, T. Vdovenkova, **A.J. Slavin,*** Trent University, Canada

The Au-Si system has been well studied as a model system for metal-silicon interfaces. In contrast, the present work is one of the few studies of the growth of a silicon-oxide film on a gold substrate. The gold is the electrode, about 200-nm-thick, of a quartz-crystal microbalance (QCM) used for measuring the deposited mass. In early work on the deposition of Si onto a Au film about 10-nm thick, Si was visible in Auger spectroscopy (AES) from the start of evaporation. In contrast, in our study the evaporation of several monolayer-equivalents of Si under UHV conditions at room temperature resulted in the Si dissolving into the gold without the accumulation of any Si on the surface. Subsequent exposure to oxygen gas did not result in the segregation of Si to the surface. However, a layer of oxide from 0.5 to 1.8 nm thick was produced by a series of evaporations of the Si in the presence of O@sub2@ gas at 1 x 10@super -5@ torr with the sample held at 78@super o@C, probably aided by oxygen ions produced at the hot filament of the evaporator. The film growth has been studied by AES and EELS, using the QCM to monitor the amount of silicon oxide deposited. The average stoichiometry of the oxide was roughly SiO@sub 1.75@, based on an AES peak position of 78 eV compared to 92 for elemental bulk Si and 76 for SiO@sub 2@. One atomic layer of Si evaporated in vacuum onto the oxide film gave an AES peak at 90 eV, thought to be elemental Si; this showed that the Si oxide acted as a barrier to Si in-diffusion. This extra Si did not oxidize at 78@super o@C under O@sub 2@ gas at 1 x 10@super -5@ torr with the evaporator filament off. The intensity of the 90-eV peak decreased in comparison with the peak for Si in SiO@sub x@, under prolonged exposure to the electron beam. This research was supported by NSERC, Canada.

11:20am **EL-WeM10 Kinetics of the Selective Oxidation of Si(100) versus W by H@sub 2@O Steam in Hydrogen***, **Y. Liu,** J. Hebb,* Axcelis Technologies, Inc.

The selective oxidation (SELOX) of Si versus tungsten (W) is an important process to form W gate electrodes on SiO@sub 2@ dielectric in the advanced CMOS devices. The SELOX was studied using a small quartz reactor, a catalytic water vapor generator (WVG), a quadrupole mass spectrometer (QMS), an ellipsometer and a 4-point probe. New kinetics data were obtained for the wet SiO@sub 2@ growth on Si(100) at 1 atmosphere and 900-1150°C, with the steam (H@sub 2@O) in H@sub 2@ percentage being 0 to 80%. A Si(100) or a W-covered Si(100) wafer was rapidly heated to a desired temperature in an inert gas. Fast gas sequencing was carried out to expose the wafer to (1) H@sub 2@ for W passivation, (2) steam+H@sub 2@ for Si oxidation and (3) H@sub 2@ for WO@sub x@ reduction. Gases in the reactor were analyzed with the QMS. The SiO@sub 2@ thickness was measured with the ellipsometer while the W film was characterized by its sheet resistance change. Preliminary results showed that the SiO@sub 2@ thickness is proportional to the steam percentage at a given set of oxidation temperature and time, suggesting that the SiO@sub 2@ growth follows the first-order kinetics. At a 20% steam percentage and during the first 60 sec, the SiO@sub 2@ growth rates at 955°C and 1047°C have been determined to be 0.96 Å/sec and 2.89 Å/sec, respectively. This yields an activation energy of 1.67 eV in agreement with the published values using O@sub 2@ or steam+O@sub 2@. Between 60 and 180 sec, the growth rates decreased to 0.73 Å/sec and 1.81 Å/sec, respectively. Hence, the earlier oxidation stage is kinetically controlled by an interface reaction step while the later stage is limited by a different slow step. Besides the detailed kinetic studies for the wet Si oxidation in the H@sub 2@ reducing ambient, systematic data will be presented for the W oxidation and WO@sub x@ reduction to explore the selectivity window for Si SELOX.

Magnetic Recording Topical Conference
Room 110 - Session MR+MI+AS+SE-WeM

Magnetic Recording: Tribology & Integration

Moderator: Y.T. Hsia, Seagate Technology

8:20am **MR+MI+AS+SE-WeM1 Nanotribology of Simple and Complex Fluids at Aqueous Interfaces@footnote 1@***, **S. Granick**,* University of Illinois, Urbana **INVITED**

Oil and lubrication are so synonymous that it is easy to discount the importance of aqueous-based lubrication -- not least in our own bodies, wich are full of surfaces in sliding contact. This talk will present recent studies of (a) the hydrophobic effect when surfaces are in relative motion, (b) modifying the boundary conditions of fluid flow, from no-slip to slip, and (c) ongoing attempts to watch single molecules under confinement. These issues of water in intimate contact with solid surfaces point the way to possible new strategies for energy-saving during fluid transport and have relevance to filtration, colloidal dynamics, and microfluidic devices.@footnote 2@ @FootnoteText@ @footnote 1@Work performed with Yingxi Zhu, John Jiang Zhao, Ashish Mukhopadhyay, and Hyungjung Lee @footnote 2@Work supported by the National Science Foundation and by the U.S. Dept. of Energy, Division of Materials Sciences under Award Number DEFG9645439 through the Frederick Seitz Materials Research Laboratory at the University of Illinois at Urbana-Champaign.

9:00am **MR+MI+AS+SE-WeM3 The Ever Changing Disk Drive Environment: Can Filter Technology Keep Pace?***, **A.J. Dallas**, J. Joriman, L. Ding, D. Arends, S.B. Miller, III,* Donaldson Co., Inc. **INVITED**

The cleanliness of the internal environment of a disk drive is critical to its reliability, performance, and longevity. As a result, we have seen particulate and chemical filters become commonplace in the design of disk drives of all types and sizes. The incorporation of chemical filters into the disk drive environment has proven to be an effective means of controlling the humidity and contamination level. Generally, silica gel is used to control the humidity level, whereas carbon and chemically-treated activated carbon are used to minimize organic and acid gas contamination levels. As disk drive technology moves into the future, chemical filtration is expected to play an ever-increasing role in the overall drive's performance. How will filter technology change to meet these requirements? This presentation will provide an overview of chemical filtration, filter design, and the current technology. In addition, we intend to focus on: 1) test methods designed to evaluate and identify internal drive contamination; 2) test methods to evaluate materials used in chemical filters; 3) chemical filter performance; 4) extending test methods and chemical filters to low contaminant concentrations; 5) targeting specific chemical species with chemical filters; 6) humidity control; and 7) the future of chemical filtration.

9:40am **MR+MI+AS+SE-WeM5 Effect of Humidity on Lubricated Carbon Overcoats***, **N. Shukla**,* Seagate Technology*; A.J. Gellman,* Carnegie Mellon University*; R. Veerdonk, X. Ma, J. Gui,* Seagate Technology

A quartz crystal microbalance has been used to measure contaminant adsorption on magnetic data storage media under controlled conditions. This apparatus has been developed to make measurements of contaminant adsorption at the level of 0.1 ng/cm2 with a time resolution on the order of seconds. Initially we have measured humidity uptake on amorphous carbon overcoats coated with lubricants. We have been able to estimate the amount of water adsorbed on lubricated carbon overcoats at room temperature and at moderate humidity levels (~ 25% RH). Adsorption and desorption is fast indicating that equilibrium with ambient humidity is reached on timescales of minutes, much faster than the timescales for fluctuations in ambient humidity. We have also studied water adsorption on different types of lubricants deposited at different thicknesses. Interestingly, the amount of water adsorbed on lubricated and unlubricated carbon overcoats is similar suggesting that water adsorption is primarily dependent on the properties of the carbon. We have studied the bonding of water on carbon overcoats and also studied bonding of lubricants on carbon overcoats.

10:00am **MR+MI+AS+SE-WeM6 Tribological Implications of the Confinement in PFPE Boundary Lubricant Films***, **G.W. Tyndall**,* IBM Almaden Research Center **INVITED**

Perfluoropolyether (PFPE) films of nominally 1.0 - 2.5 nm are commonly utilized by the magnetic recording industry to lubricate the head/disk interface in hard-disk drives. In this film thickness regime, the surface of the magnetic recording disk will "energetically confine" the lubricant. This confinement is manifested in physical and mechanical properties of the PFPE lubricant that differ substantially from those of the bulk fluid. In the current talk, the experimental evidence for confinement in the PFPE/carbon system will be reviewed, and the implications to the tribology of the head-disk interface discussed.

10:40am **MR+MI+AS+SE-WeM8 Pushing Perfluoropolyether Molecules Across Surfaces Using Air Shear***, M.A. Scarpulla, **C.M. Mate**,* IBM Almaden Research Center

We have investigated the surface mobility of thin films (<5 nm thick)of linear chain perfluoropolyether polymers on silicon and CN@sub x@ surfaces while subjecting them to air shear stresses. These experiments are elucidating the nature of viscosity in molecularly thin films of lubricants important for magnetic recording. For polymer chains with neutral CF@sub 3@ end groups, we find that the effective viscosity is close to the bulk viscosity even at sub-monolayer coverage. The addition of alcohol end groups to the polymer chains acts to anchor the first layer of molecules to a surface, greatly increasing the effective viscosity relative to the bulk. For the second layer, the alcohol-terminated polymers exhibit effective viscosities near their bulk viscosity, while dewetting is observed in thicker films.

11:00am **MR+MI+AS+SE-WeM9 Kinetics and Energetics of the Desorption of Polyether Lubricants***, **K.R. Paserba**, N. Prashanth, A.J. Gellman,* Carnegie Mellon University

Desorption or evaporation is one of the mechanisms for loss of perfluoropolyalkylether (PFPE) lubricants from the surfaces of data storage media. One approach to minimizing PFPE loss by desorption is the use of lubricants with increasing molecular weight or increasing average chain length. In order to understand the effects of chain length on the lubricant evaporation kinetics we have studied the desorption kinetics of monolayer films of oligomeric ethers with varying chain length adsorbed on the surface of graphite. This study has used monodispersed samples of oligomeric ethyleneglycol dimethylethers, CH3O(CH2CH2O)mCH3, and oligomeric ethyleneglycols, HO(CH2CH2O)mH, as models for the perfluoropolyalkylether lubricants Fomblin Z and Fomblin Zdol. Their adsorption and desorption from the surface of graphite has been measured as a function of chain length, M = 3m+3, or molecular weight by using thermally programmed desorption methods in ultra-high vacuum. The results of these measurements show the surprising result that the desorption energies, @DELTA@E@sub des@, are non-linear in the chain length. What is most interesting is that the desorption energies can be expressed by the power law expression @DELTA@E@sub des@ = a + b M@gamma@ with @gamma@ ~ 0.5. A model has been proposed for the desorption mechanism of such oligomeric lubricants from surfaces which can quantitatively reproduce the dependence of the desorption energies on chain length. The origin of the non-linearity is the conformational isomerism of the oligomers as they desorb from the surface. We will discuss the implications of these results on the desorption of oligomeric PFPE lubricants from the surfaces of magnetic data storage media.

11:20am **MR+MI+AS+SE-WeM10 Ramp Materials Challenges with Load/Unload Technology***, **B. Hiller**,* Maxtor Corporation **INVITED**

Dynamic ramp load/unload technology (or short: ramp load) is replacing contact start/stop technology in hard disk drives. Key reasons are superior shock performance and improved reliability. Ramp load adds a new part to the drive (the ramp) and a new interface (between ramp and suspension lift tab). Proper selection of the ramp material and specification of the ramp/tab interface are key to drive reliability. This talk will address the important issues and will present state-of-the art solutions, as well as an outlook on future developments. As with all in-drive materials, minimal chemical outgassing is required. After that, the most important criteria for the ramp material are low friction and wear, and adequate mechanical stability. Out of a large number of candidate materials, only two materials are primarily used in today's products: Teflon-filled liquid crystal polymer (LCP) and acetal homopolymer (POM). These two materials optimize the materials issues in different ways and have their unique application range. LCP excels at mechanical stability, while POM exhibits superior tribology. Surface roughness affects friction and wear and needs to be controlled for both sliding partners, but control is more crucial for the much harder stainless steel suspension lift tab. Current products employ both spherical and cylindrical lift tab shapes. The relative merits of both approaches will be discussed. Tribological and mechanical properties are so multi-faceted that a large portion of this talk will be devoted to presenting measurement techniques and key results. Other important properties such as electrostatic charging and cost will also be addressed.

Nanotubes: Science and Applications Topical Conference Room 133 - Session NT-WeM

Nanotubes: Nanoelectronics

Moderator: L. Samuelson, Lund University, Sweden

8:20am **NT-WeM1 When are Carbon Nanotubes Ballistic Conductors?**, ***W.A. de Heer,*** Georgia Institute of Technology **INVITED**

Frank, de Heer et al (Science 280,1744 (1998) found that freely suspended multiwalled carbon nanotubes (MWNTs) are 1-D conductors; the current flows on the outer layer, while large current densities are sustained. Quantized conductance was also found. These findings imply that carbon nanotubes could be ballistic conductors at room temperature. However there are difficulties that need clarification. One is that the conductance is only half what is expected from the theory of single wall nanotubes. Experiments performed on substrate supported and lithographically contacted nanotubes do not (yet) exhibit quantized conductance. Moreover electrical transport in carbon nanotubes is still quite confusing. Our experiments show that the conductance of clean, well-contacted nanotubes is quantized and independent of intercontact distance. Contamination, defects, non-ideal contacts and substrate interactions may explain the discrepancies between our experiments and others.

9:00am **NT-WeM3 Electrical Characterization of Carbon Nanotube - Metal Contacts**, ***R. Vajtai***, *B.-Q. Wei, Y.V. Shusterman,* Rensselaer Polytechnic Institute; *K.A. Dunn, K. Dovidenko,* The University at Albany-SUNY; *L.J. Schowalter, P.M. Ajayan,* Rensselaer Polytechnic Institute

Carbon nanotubes are excellent candidates to be used as interconnects or even active elements in nano-electronics. To harness the electrical properties of nanotubes in future nano-circuits, one needs to handle the most local neighboring effects such as contacting, insulation from the substrate and localized charges on the surface. Here we present results on spatially resolved electronic conductance of multiwalled nanotubes and nanotube networks on samples prepared by conventional and focused ion beam (FIB) lithography. Our results show that electrical potential changes along the nanotubes, drop at the contacts and spread into the perpendicular direction causing measuring difficulties for the nanoprobe, but also causing changes in the local electric field sensed by the nanotube. In this talk we will present the topographic and related spatially resolved electrostatic potential distribution in nanotube networks and we will describe the possible effect on the applications of nanotube-metal and nanotube-nanotube interconnects. Investigations made on similar configurations also showed long-term, high-current durability of the system, and low noise-factors resulting in most probably from the good coupling between the nanotubes and the metal electrodes.

9:20am **NT-WeM4 Analysis of Carbon Nanotube Metal-Semiconductor Diode Device**, ***T. Yamada,*** NASA Ames Research Center

We study recently reported drain current (I@sub d@)-drain voltage (V@sub d@) characteristics of a carbon nanotube metal-semiconductor diode device with the gate voltage (V@sub g@) applied to modulate the carrier density in the nanotube.@footnote 1@ The diode was kink-shaped at the metal-semiconductor interface. It was shown that (1) larger negative V@sub g@ blocked I@sub d@ more effectively in the negative V@sub d@ region, resulting in the rectifying I@sub d@-V@sub d@ characteristics, and that (2) positive V@sub g@ allowed I@sub d@ in the both V@sub d@ polarities, resulting in the non-rectifying characteristics. The negative V@sub d@ was the Schottky reverse direction, judging from the negligible I@sub d@ behavior for a wide region of -4 V < V@sub d@ < 0 V, with V@sub g@ = -4 V. Such negative V@sub g@ would attract positive charges from the metallic electrodes (charge reservoir) to the nanotube and lower the nanotube Fermi energy (E@sub F@). With larger negative V@sub g@, the experiment showed that the Schottky forward direction (V@sub d@ > 0) had a smaller turn-on voltage and the Schottky reverse direction (V@sub d@ < 0) was more resistant to the thermionic breakdown. Therefore, the majority carriers in the transport would be electrons since they can see a lower tunneling barrier (shallower built-in potential) in the forward direction when E@sub F@ is lowered, and a thicker tunneling barrier (Schottky barrier) in the reverse direction due to the reduction in the electron density when E@sub F@ is lowered. @FootnoteText@ @footnote 1@Z. Yao, H. W. Ch. Posma, L. Balents, and C. Dekker, Nature 402, 273 (1999).

9:40am **NT-WeM5 Electrical Transport through Vertically Aligned In-situ Contacted Multiwall Carbon Nanotubes**, *F. Kreupl,* ***A. Graham,*** *E. Unger, M. Liebau, W. Hönlein,* Infineon Technologies, Corporate Research, Germany

In order to exploit the high electrical performance of carbon nanotubes (CNTs), they have to be connected at both ends with highly conductive, i.e., metallic contacts. In addition to the quality of the grown CNTs, it is also very important that the contact resistances are as low as possible. CNTs grown on metallic surfaces give inherently a low contact resistance as the catalyst particles from which the nanotubes grow out of contact almost all layers of the multi-wall CNTs. We will report on electrical transport measurements on arrays of vertically aligned multi-wall CNTs contacted at the top and bottom. The bottom electrode with catalyst particles is covered completely with a thick silicon dioxide layer, in which holes of various sizes are etched down to the bottom electrode with reactive ion beam etching. The holes serve as templates in which CNTs are grown with chemical vapor deposition (CVD) directly from catalyst particles at the bottom electrode and contacted on top with a second metal electrode. Electrical measurements of the CNTs yielded extremely low resistances indicating electrical transport through almost all shells of the individual CNTs.

10:00am **NT-WeM6 Electronic Rectification, Ballistic Switching, and Logic Gates with Carbon Nanotube `Y-Junctions'**, ***D. Srivastava,*** NASA Ames Research Center; *A. Andriotis,* Foundation for Research and Technology, Greece; *M. Menon,* University of Kentucky; *L. Chernozetonski,* Russian Academy of Sciences, Russia

I-V characteristics of single-wall carbon nanotube Y-junctions are calculated using an efficient embedding Green's Function formalism that allows for conductance across nanotube multiple junctions and realistic nanotube metal-lead contacts. The current vs voltage characteristics show the assymetry and rectification, in agreement with recent experimental results on multiwall nanotube Y-junctions. In symmetric Y-nanotube junctions the rectification has a weak dependence on the angle at the junction, and can support both ballistic rectification and/or ballistic switching operating modes. Although structural symmetry of the Y-junction is found to be necessary condition for rectification, it may not be sufficient for all cases. Transport calculations as a 3-terminal device show modulation of the current in the bias channel and a branch as a fucntion of applied voltage across the other branch. This behavior has been exploited to propose simple logic gates with Y junction carbon nanotubes.

10:20am **NT-WeM7 Development of N-type Carbon Nanotube Transistors and Fabrication of the First Nanotube Logic Circuits**, ***V. Derycke***, *R. Martel, Ph. Avouris,* IBM T.J. Watson Research Center

Single carbon nanotubes can be used as the active channel in field effect transistors (FETs).@footnote 1,2@ Without any special treatment, the obtained FETs are always P-type: the current carriers are holes and the devices are off for positive gate bias. Here we show that this transistor behavior is due to a strong pinning of the Fermi level at the valence band of the semiconducting nanotubes and the presence of a large Schottky barrier for electron injection into the device. The fabrication of N-type FETs has recently been achieved by doping the device with an electron donor such as potassium.@footnote 3@ We introduce a novel approach of converting SWNT-based P-FETs into N-FETs without the use of dopands. The technique relies on the control of the electrostatic barriers and the modification of the contacts. By a specific treatment of the device we can position the Fermi level at any position within the band gap in a controlled manner and therefore modify the character of the device. For intermediate modification, the Fermi level lies in the middle of the band gap and the device shows both hole and electron conduction at negative and positive gate biases respectively. In completely converted devices, the Fermi level is pinned at the conduction band edge and the resulting FET is fully N-type. Using our ability to prepare both P- and N-type transistors we were able to fabricate the first nanotube-based integrated logic circuit, a "NOT" gate (voltage inverter). Inverters using K-doped tubes were also fabricated. We will compare the voltage inverters made by the two techniques. @FootnoteText@ @footnote 1@ S. J. Tans, A. R. M. Verschueren, and C. Dekker, Nature (London) 393, 49 (1998). @footnote 2@ R. Martel, T. Schmidt, H. R. Shea, T. Hertel, and Ph. Avouris, Appl. Phys. Lett. 73, 2447

(1998). @footnote 3@ M. Bockrath, J. Hone, A. Zettl, P.L. McEuen, A.G. Rinzler and Richard E. Smalley, Phys. Rev. B 61, R10606 (2000).

11:00am **NT-WeM9 Contacting Carbon Nanotubes by Electrodeposition of Metal*, D.W. Austin*,** *M.A. Guillorn,* University of Tennessee*; D.B. Geohegan,* Oak Ridge National Laboratory*; A.A. Puretzky,* University of Tennessee*; P.F. Britt, M.L. Simpson,* Oak Ridge National Laboratory

We report our progress on the development of controllably contacting carbon nanotubes as part of our efforts to develop molecular-scale electronic devices. We are applying two approaches for electrically contacting single wall carbon nanotubes (SWNTs) that span metal electrodes. In the first approach, electrode metal is evaporated over the nanotubes, at the risk of damaging the tubes with the patterning electron beam. The second approach is to deposit the SWNTs onto prefabricated electrodes and then locate nanotubes that bridge two or more contacts. In the latter method, the nanotube/electrode resistance is typically on the order of 1 M@ohm@, due to the high contact resistance between the electrode and the sidewall of the nanotubes. We have had success in depositing SWNTs across prefabricated electrodes and making charge transport measurements. Our next step is to establish a contact method that will improve the conductivity across the nanotube/metal junction, and lead to the development of SWNT-based devices. We are conducting a set of experiments to determine if nanotubes can be contacted by electroplating metals such as gold, palladium, and platinum onto existing electrodes. In this approach, the electrodeposition of metal takes place long enough to allow the electrodes to contact the ends of the SWNTs. We will report the results of our electrodeposition experiments and describe our ongoing efforts towards the development of carbon nanotube-based molecular electronic devices.

Organic Films and Devices
Room 131 - Session OF+NS+SS+BI-WeM

Self Assembled Monolayers/Ordered Films

Moderator: R. Maboudian, University of California, Berkeley

8:20am **OF+NS+SS+BI-WeM1 Preparation and Characterization of Nano-Scale Mixed Self-Assembled Monolayers***, S. Chen, L. Li, C. Boozer,* ***S. Jiang,*** University of Washington

Fabrication of nano-scale structures by mixed self-assembled monolayers (SAMs) has recently attracted much attention due to its scientific importance and potential applications to chemical and biological sensors, and biocompatible materials. However, it is still difficult to prepare nano-scale mixed SAMs since phase segregation occurs when two components are quite different. Recently, we proposed a new kinetically-trapped method to prepare nano-scale uniform mixed SAMs. In this work, we prepared various mixed SAMs, such as dodecanethiol(C12)/octanethiol(C8), tetradecanethiol (C14)/C8, 11-mercaptoundecanol(C11OH)/C8, and 11-mercaptoundecanoic acid(C10COOH)/C8 at a range of compositions using the kinetically-trapped method. Our results by low-current scanning tunneling microscopy (STM) revealed homogenous mixed SAMs with various terminal groups and a solution composition up to 25% of long chains formed at higher solution temperatures. Possible mechanism for forming uniform mixed SAMs will be discussed.

8:40am **OF+NS+SS+BI-WeM2 The Role of Linker Molecules in the Controlled Adsorption of Polystyrene (PS) Nano Particles***,* ***M. Himmelhaus,*** Universität Heidelberg, Germany*; H. Takei,* Hitachi Central Research Laboratory, Japan

Controlled adsorption of PS nano particles onto specific regions of flat surfaces has found increasing interest as potential applications for surface-adsorbed PS particles, such as fabrication of quantum dots, optical switches, mesoscopic lasers, biosensors, as well as dosing of biomolecules, require an easily applicable adsorption scheme capable of addressing macroscopic areas. Among the various techniques those utilizing linker molecules to promote particle-particle as well as particle-surface interaction have only recently been applied as to date the role of the linker molecules in the various physical and chemical adsorption mechanisms is only poorly understood. We have studied the effect of several water-soluble linker molecules on the adsorption behavior and packing density of surfactant-free polystyrene latex spheres from suspension. By variation of several parameters, such as molarity of the linker molecules, pH of the suspension, as well as choosing differently functionalized PS particles we can distinguish several adsorption mechanisms from each other, reaching from purely physical ones to covalent bonding. This basic study is a first step to the fabrication of 2D crystalline monolayers of macroscopic lateral extension by means of chemically driven self-assembly.

9:00am **OF+NS+SS+BI-WeM3 Characterization of Biphenyl-substituted Alkanethiol Self-assembled Monolayers by High-resolution X-ray Photoelectron Spectroscopy***, K. Heister, H.-T. Rong, M. Buck,* University Heidelberg, Germany*; L.S.O. Johansson,* University Karlstad, Sweden*;* ***M. Zharnikov****, M. Grunze,* University Heidelberg, Germany

Synchrotron-based high resolution X-ray photoelectron spectroscopy was applied to characterize self-assembled monolayers (SAM) of biphenyl-substituted alkanethiols CH@sub 3@(C@sub 6@H@sub 4@)@sub 2@(CH@sub 2@)@sub n@SH (BPn, n = 1-4) on Au and Ag substrates. Beyond previously identified odd-even changes in the packing density and the tilt angle of the biphenyl moieties, the high resolution spectra reveal a number of additional odd-even effects upon variation of the number of methylene groups in the aliphatic part in the BPn molecule. Their occurrence and mutual correlation suggests that a BPn SAM represents a strongly correlated, highly ordered molecular assembly. In particular, periodical changes of a shake-up feature in the C 1s region are observed, which are related to the differences in the arrangement of the aromatic matrix. The width and binding energy of the S 2p signals also exhibit odd-even changes. The width changes are associated with the occupation of either equivalent or non-equivalent adsorption sites on the polycrystalline (111) Au and Ag substrates. The comparison of the width values with those for conventional alkanethiols implies that the substrate bonding of alkanethiols on gold cannot be described by a single adsorption site. At the same time, the FWHM of the S 2p@sub 3/2,1/2@ peaks in the loosely packed BPn/Au (~0.50 eV) was found to be the smallest one among all thiol-derived SAMs investigated by HRXPS until present. Therefore, this value can be associated with the occupation of equivalent adsorption sites on the Au(111) surface. This work has been supported by the German BMBF (05 SF8VHA 1 and 05 SL8VHA 2), DAAD (313/S-PPP), and DFG (Bu820/11-2).

9:20am **OF+NS+SS+BI-WeM4 Separation via Self-assembly of Enantiomers of Chiral Aromatic Hydrocarbons Adsorbed on Metal Surfaces***,* ***K.-H. Ernst,*** *Y. Kuster, R. Fasel,* EMPA Duebendorf, Switzerland

We studied the interaction of heptahelicene ([7]H), a helically shaped, polyaromatic phenanthrene derivative, with well-defined single-crystal metal surfaces under ultra high vacuum (UHV) conditions. The molecules, racemate as well as the pure enantiomers, were deposited via molecular beam technique and subsequently characterized with surface sensitive techniques like temperature programmed desorption (TPD), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), scanning tunneling microscopy (STM), time-of flight secondary mass spectrometry (ToF-SIMS), X-ray absorption spectroscopy (NEXAFS), and X-ray photoelectron diffraction (XPD). On Ni(111), the [7]H-molecule is adsorbed intactly at room temperature. TPD, however, shows only desorption of molecular [7]H from the multilayers. The first layer undergoes decomposition into carbon and hydrogen at 650 K. From Cu(111), molecular desorption is also observed at low coverages. The closed packed monolayers of [7]H on Ni(111) and Cu(111) show two-dimensional lattice structures. Adsorption of racemic [7]H leads to self-alignment into domaines on the surface, which are mirror images of each other. This is not observed after exposure to pure enantiomers and can be explained with a lateral separation of the enantiomers into homochiral domaines on the surface. For the pure M-enantiomer on the stepped Cu(332) surface, an azimuthal alignment of the molecular spirals is observed. Models for the monolayer structures and the mechanism of the separation will be discussed. Support by the Swiss National Science Foundation (NFP 36) is gratefully acknowledged.

9:40am **OF+NS+SS+BI-WeM5 Mesoscopic Correlation of Supramolecular Chirality in One-Dimensional Hydrogen-Bonded Assemblies***,* ***J.V. Barth,*** Ecole Polytechnique Federale de Lausanne, Switzerland*; J. Weckesser,* Max-Planck-Institut fuer Festkoerperforschung, Germany*; A. De Vita,* Institut Romand de Recherche Numerique en Physique des Materiaux, Switzerland*; C. Cai,* University of Houston*; K. Kern,* Max-Planck-Institut fuer Festkoerperforschung, Germany

We studied enantioselective self-assembly in two dimensions employing the molecule 4-[trans-2-(pyrid-4-yl-vinyl)] benzoic acid. Scanning tunneling microscopy observations at noble metal surfaces reveal the formation of hydrogen-bonded supramolecular twin chains in two mirror-symmetric species, each containing only molecules of a given chirality. The twin chains are ordered in µmm-gratings, where a mesoscopic correlation of supramolecular chirality over the entire domain size without intimate molecular contact persists. This novel phenomenon reflects mesoscopic chiral segregation due to chiral recognition in the formation of the supramolecular assemblies. Theoretical modelling in conjunction with direct observations indicate that twin chains act as enantioselective templates for transient molecular attachment, which process mediates self-replication of supramolecular chirality and the enantiopure gratings' evolution.

10:00am **OF+NS+SS+BI-WeM6 Controlling Molecular Orientation in Solid Films Via Self-organization in the Liquid-crystalline Phase***, I.K. Iverson, S.-W. Tam-Chang,* ***S.M. Casey,*** University of Nevada, Reno*; B.A. Pindzola,* University of California, Berkeley

We report the control of molecular orientation in solid films through self-organization and induced-orientation processes. We synthesized water-soluble cationic 3,4,9,10-perylene diimide (1) and studied its self-organization in aqueous solution. By UV-vis spectroscopy, H-aggregates of 1 are observed forming in solutions with concentrations as low as 10@super -7@ M. At concentrations above approximately 0.1 M (7% w/w) these solutions are observed with polarized microscopy to form a chromonic N phase (a nematic lyotropic liquid crystalline phase) at room temperature. Upon induced alignment (by shearing) of the chromonic N phase on a glass substrate and removal of solvent, anisotropic solid films of the dichroic dye are produced. These films have dichroic ratio values that routinely exceed 25 and in some cases 30, making them excellent sheet polarizers over the blue and green region. Using a combination of polarized UV-vis and FT-IR spectroscopies, the orientation of the average molecular plane in these films is determined to be perpendicular to both the shearing direction and the substrate plane. X-ray diffraction studies indicate that the molecules in the solid film possess a high degree of order.

10:40am **OF+NS+SS+BI-WeM8 Effect of Lipid Vesicle Fusion on the Ordering and Redox Activity of 11-(ferrocenyl carbonyloxy) Undecanethiols Self-assembled Monolayers***, A.T.A. Jenkins,* University of Bath, U.K., Great Britain*;* ***J.F. Le Meur,*** University of Bath, U.K.

Self-assembled Monolayers (SAMs) of 11-(ferrocenyl carbonyloxy) undecanethiol were made following a procedure given by Chidsey et @footnote 1@ The formation of the 11-(ferrocenyl carbonyloxy) undecanethiol SAM on gold was followed in-situ by Surface Plasmon Resonance (SPR)and showed a film of thickness 13 Å was formed. Impedance measurements indicated a high level of film coverage. Cyclic voltammetry was subsequently used to electrochemically characterise the SAM, and check its stabilty with respect to immersion in electrolyte. Egg-Phosphatidylcholine lipid vesicles were created by extrusion through a 50 nm membrane and were adsorbed on the SAM. SPR was used to follow the lipid adsorption on the SAM. Cyclic voltammetry measurements on the SAM-lipid system showed a large and reproducible increase in the peak anodic and cathodic currents after lipid adsorption, although the total quantity of charge transfered stayed the same. This is likely to be due to an increase in order of the ferrocene units in the SAM, allowing for a faster transfer of electrons on the lipid covered SAM than the SAM alone. The above experiments were repeated with binary mixtures of SAMs containing both 11-(ferrocenyl carbonyloxy) undecanethiol and mercaptoundecanol moities. It was found that the increase in anodic and cathodic current maximums measuresed by cylic voltammetery was disproportionately lower than the single component SAM (relative to the coverage). From this we propose a model for how the SAM structure changes upon lipid adsorption. @FootnoteText@ @footnote 1@ Chidsey, C.E.D.; Bertozzi, C.R.; Putvinski, T.M.; Mujsce, A.M. Journal American Chemical Society, 1990, 112, 4301-4306.

11:00am **OF+NS+SS+BI-WeM9 Temperature-dependent Morphology of Crystalline p-sexiphenyl Thin Films on KCl(001)***,* ***E.J. Kintzel, Jr.,*** Florida State University*; D.-M. Smilgies,* Cornell University*; J.G. Skofronick, S.A. Safron,* Florida State University

Investigations of the morphology of ultrathin films of p-sexiphenyl (p-6P) vapor deposited onto KCl(001) have been carried out using the complementary techniques of X-Ray Diffraction (XRD) and Atomic Force Microscopy (AFM). XRD studies have shown that the molecular orientation of the p-6P is dependent on the substrate temperature during deposition. For films prepared at low temperatures, the p-6P molecules take a lying orientation, with the long axis of the molecule aligned parallel to the substrate. As the substrate temperature was increased during deposition, XRD results indicate two coexisting molecular orientations, corresponding to lying and standing p-6P molecules. AFM images provide independent confirming evidence of the influence of substrate temperature on molecular orientation, consistent with the XRD results.

11:40am **OF+NS+SS+BI-WeM11 Characterization of Photoisomerization Reaction of Azobenzene-contanining SAMs: Reaction Kinetics and Thermal Stability***,* ***K. Tamada,*** National Institute of Advanced Industrial Science and Technology (AIST), and Frontier Research System, RIKEN, Japan*; H. Akiyama, T. Wei,* AIST, Japan

We studied the change of photoreactivity of azobenzene disulfide SAMs under thermal stress. Azobenzene-containing unsymmetrical disulfide (C6AzSSC12) SAM was annealed at each temperature (70, 85, 100, 120, 140°C) for 1 hr, then the photoreaction was monitored with surface plasmon resonance spectroscopy (SPR) in hexane. The photoreaction was stable under 100°C when no decomposition of adsorbed molecules was detected, while it was suddenly reduced at over 100°C when the decomposition was taking place. After annealing at 140°C, the reactivity of the unsymmetrical disulfide SAM reached to the level of the corresponding azobenzenethiol SAMs (single component), suggesting the phase segregation of the adsorbed molecules by annealing. We designed new azobenzene thiol/disulfides (C6Az(Me)thiol, C6Az(Me)SSC12) to achieve more thermally stable photoresponse. In these molecules, CH@sub 3@-group is introduced to the azobenzene ring directly to avoid dye aggregation sterically. The C6Az(Me)thiol SAM exhibited much higher photoreactivity than conventional azobenzenethiol, which suggests that dye functions are less aggregated even in the single component SAMs. The C6Az(Me)SSC12 exhibited much higher photoresponse compared with C6AzSSC12 after annealing, since these azo dyes can react even in phase segregated domains. We also discuss photoisomerization reaction kinetics (cis to trans, trans to cis) in correlation with dye alignment.

Plasma Science
Room 103 - Session PS1-WeM
Dielectric Etch II

Moderator: E.S. Aydil, University of California, Santa Barbara

8:20am **PS1-WeM1 Plasma Etching of High Dielectric Constant Materials***,* ***L. Sha,*** *J.P. Chang,* University of California, Los Angeles

Novel plasma etching chemistries are needed to pattern high dielectric constant materials, such as transition metal oxides, to enable their integration in sub-0.13µm complementary metal oxide semiconductor (CMOS) devices. In the work, we aim to study the reaction kinetics of etching zirconium oxide thin films in a high-density chlorine discharge. An Electron Cyclotron Resonance (ECR) microwave reactor is used to generate a chlorine discharge for etching ZrO@sub 2@. The plasma properties, such as the electron density, temperature and distribution, are determined by a Langmuir probe. A gridded ion energy analyzer is built to monitor the ion flux, impinging energy, and distribution. Optical emission spectroscopy (OES) and quadrupole mass spectroscopy (QMS) are employed to identify the gas phase reactive species, including the reactants (Cl@sub 2@, Cl, Cl@super +@, Cl@super -@, ...) and the reaction products (ZrCl@sub x@, ZrO@sub x@, ...), and quantify their concentrations as a function of the chlorine pressure, substrate temperature, substrate bias, and the plasma source power. Surface reaction chemistry and the etching rate are determined by in-situ transmission infrared spectroscopy and laser interferometry. The reactant neutral to ion flux ratio, a strong function of the processing pressure and the input microwave power, is a key factor affecting the surface reaction chemistry and the etching anisotropy. The concentrations of various ZrCl@sub x@ with different x values are measured and showed a strong dependency on both the reactant neutral to ion flux ratio and the ion incident energy. The surface roughness of the silicon substrate after etching is measured by AFM and compared to that of a pristine silicon surface. The results indicate that the roughness is preserved with lower ion energy, and suggest that the substrate bias should be minimized near the end point.

8:40am **PS1-WeM2 Low-k Etch Selectivity Enhancement Through Ion Energy Control***,* ***R. Silapunt,*** *A.E. Wendt,* University of Wisconsin-Madison*; K.H.R. Kirmse, F.G. Celii,* Texas Instruments, Inc.

Organosilicate glass (OSG) is a low-k dielectric material under development for high speed interconnects in integrated circuit manufacturing, but selective etching of OSG over etch stop layers, Silicon Carbide (SiC) and Silicon Nitride (SiN), has proven challenging. Because the energy of ions bombarding the substrate has been shown to play an important role in etch selectivity, it has been proposed that improved ion energy control may provide a solution for improving OSG etch selectivity. However, the conventional sinusoidal substrate bias voltage waveform leads to a broad ion energy distribution (IED), allowing only crude control over average ion energy. Using a narrow IED may significantly enhance selectivity, especially when the ions have energy above the etching threshold energy of one material, but below the threshold energy of the other. We have applied a technique for producing a narrow IED to evaluate its potential for improving OSG/SiN and OSG/SiC etch selectivity. This method replaces the sinusoidal substrate bias voltage waveform with a specially tailored bias voltage waveform consisting of a short voltage spike in combination with longer periods of constant voltage. This produces a nearly constant voltage drop across the substrate sheath and thus a narrow IED. Etching experiments have been conducted in a helicon plasma etching reactor with a C@sub 4@F@sub 8@/Ar/N@sub 2@ gas mixture. A comparison of OSG/SiC and OSG/SiN selectivities between sinusoidal and tailored substrate bias voltage waveform has been made. Etch rates as a function of average ion energy for sinusoidal and tailored bias voltage waveforms show significant differences. With the tailored bias voltage waveform, infinite selectivity is achieved for a 40 V range of bias voltage, while a maximum selectivity of ~2:1 is achieved for the sinusoidal waveform.

9:00am **PS1-WeM3 Organic Low-k Film Etching in Inductively Coupled Plasma Employing N@sub 2@/H@sub 2@ and N@sub 2@/NH@sub 3@ Gases***, H. Nagai,* Nagoya University, Japan*; M. Hiramatsu,* Meijo University, Japan*; M. Hori, T. Goto,* Nagoya University, Japan

An organic low-k film, FLARE, is one of the most prospective candidates for interlayer films with lower dielectric constants (low-k). N@sub 2@/H@sub 2@ and N@sub 2@/NH@sub 3@ plasmas have been used for etching organic low-k film without degrading the film quality and etch profile. In this study, the organic low-k film was etched in inductively coupled high-density plasmas (ICP) employing N@sub 2@/H@sub 2@ and N@sub 2@/NH@sub 2@ gases. By changing the mixing ratio of these gases, the anistropic etching profile was obtained. The etching plasmas were evaluated by quadruple mass spectroscopy (QMS), optical emission spectroscopy (OES) technique and microwave interferometer. Furthermore, absolute densities of H and N radicals were measured using the vacuum ultraviolet absorption spectroscopy (VUVAS) employing micro-plasma as light source. N and H radical densities were estimated on the order of 10@super 11@ - 10@super 12@ cm@super -3@ and 10@super 12@ - 10@super 13@ cm@super -3@, respectively. It was found that the behaviors of H and N radical densities were dependent on H and N atom ratio of feed gases, and were not related to the kind of gases in N@sub 2@/H@sub 2@, N@sub 2@/NH@sub 3@. The behavior of etch rate corresponded to that of H radical density. The correlation between the behavior of radical, ion and electron densities and the etching characteristics of organic low-k film is investigated. On the basis of these results, the mechanism for anisotropic etching and the surface reaction of radicals on organic low-k film are discussed.

9:20am **PS1-WeM4 Study of Surface Reaction on Organic Low-k Dielectric Etching By Plasma Beam Irradiation***, **Y. Yamaoka**, K. Kurihara, K. Karahashi, M. Sekine, M. Nakamura,* ASET, Japan

Etching of low-k dielectrics is one of the most critical processes for the next ULSI fabrication. Etching mechanism of a poly arylene ether (PAE), which is one of the organic low-k dielectrics, was investigated by using a plasma beam irradiation apparatus. The apparatus can control ion flux density (@GAMMA@i), neutral flux density (@GAMMA@n) and ion energy (Ei), independently. The controlled plasma beam was irradiated to the PAE coated on Si substrate in an irradiation chamber, and etch rates (ERs) and desorbed products were measured. The beam was extracted from an ECR type plasma chamber with a N@sub 2@ gas. The @GAMMA@i was controlled by changing the ion beam diameter using an electrostatic focusing lens. The @GAMMA@n was changed by altering the distance between the plasma chamber and the substrate. The Ei was adjusted by DC bias applied to the plasma chamber. Pressures in the plasma and the irradiation chamber were 4 mTorr and 1 x 10@super -6@ Torr during the beam irradiation, respectively. The dominant species in the incident beam were N@sub 2@ and N@sub 2@@super +@. The ER measurements were performed at an incident angle of 0° to the substrate surface normal (@theta@ = 0°). The ERs increased with increasing @GAMMA@n at the constant @GAMMA@i and Ei. The increase of ERs could be attributed to that of the @GAMMA@n. When @GAMMA@i and @GAMMA@n were kept constant, higher ERs were obtained at higher Ei in the range from 500 to 700 eV. Desorbed species of m/e < 100 during the beam irradiation with @theta@ = 50° were measured by a quadruple mass spectrometer. Signals of m/e = 26 (CN), 27 (HCN) and 52 (C@sub 2@N@sub 2@) were observed as etched products directly desorbed from the substrate surface. Effects of H@sub 2@ gas addition on the desorbed products formation and the ERs will be discussed. @FootnoteText@ This work was supported by NEDO.

9:40am **PS1-WeM5 Low K Porous Silica Etch Behavior in Inductively Coupled Discharges***, **M. Barela**,* University of New Mexico, U.S.*; H.M. Anderson,* University of New Mexico

Low k dielectric films are of interest to the semiconductor industry as a part of the overall solution to minimize RC time delays in the ever-shrinking critical dimensions in modern semiconductor products. We have examined the etching characteristics of several representative porous silica surfaces in an industrially relevant high-density, low-pressure fluorocarbon plasma environment. These characteristics include etch rate, selectivity to Si and photoresist, etch isotropy, and etch stop. We determined that the bias power strongly influences etch rate and selectivity. It was found that the surface-plasma interaction has a strong effect on the growth of the thin fluorocarbon film which is known to mechanistically to control the etch process under optimal conditions of high etch rate and good selectivity to other materials. Furthermore, the porous nature, and modified chemical structure of the silica film has unique interactions with the etching plasma. We determined that porous silica films, where hydroxyl groups terminate surface sites, require higher bias in order to etch in comparison to similar porous silica films, which have been fluorinated. The hydroxylated surface scavenges fluorine creating a carbon rich polymer film which leads to premature etch stop and increased aspect ratio dependence etching (ARDE). FTIR and IRLAS were used to illuminate key differences in the modified surface and gas phase species in the plasma, as compared to conventional dense silica.

10:20am **PS1-WeM7 Etching Mechanism in High-aspect-ratio Contact Hole Etching***, N. Negishi, M. Izawa, K. Yokogawa, Y. Momonoi, H. Kawahara, S. Tachi,* Hitachi Ltd., Japan*; **J. Ghormley**,* Hitachi America Ltd.

As it advances beyond the 0.1-µm design rule, ULSI fabrication will require highly selective contact hole etching with high aspect ratio of over 15 and a bowing-free etched shape. To meet these requirements, the etching mechanism in high-aspect-ratio contact hole was investigated in terms of the transport of radical in a hole by using ultra-high-frequency ECR (UHF-ECR) plasma etching system@footnote 1@ with an Ar/C @sub 5@F@sub 8@/O@sub 2@ gas mixture. In this investigation, we assumed the dissociation species in this plasma are CF@sub 2@, C, F, and O. Under this assumption, almost no protective film is formed on the middle part of the hole sidewall and bowing occurs around this point. To accumulate a protective sidewall film, we increased the amount of CF@sub x@ radicals whose sticking-coefficient is low and reduced the sticking-coefficient of C radicals, so the bowing was reduced by 73%. Moreover, the distribution of C intensity was found to have a peak at a sidewall aspect ratio of around 4 in an etched hole by auger electron spectroscopy. This result can be explained by taking account of the transport of high-sticking-coefficient radicals such as C, deposition removal by O and F radicals, and radical reflection at the sidewall in a hole. Thus, we consider that the unexpected etch-stop occurs at an aspect ratio of around 4 when oxygen flow rate or ion energy is a little low. However we found that a contact hole can be formed without etch-stop and mask selectivity can be improved by step etching, during which oxygen flow rate was reduced at an aspect ratio of over 4. Accordingly, a 0.09-µm-diameter contact hole with an aspect ratio of 22 and a resist mask selectivity of over 13 was formed directionally. @FootnoteText@ @footnote 1@ K. Yokogawa, N. Negishi, S. Yamamoto, K. Suzuki, and S. Tachi, 1997 Dry Process Symp., pp 379-383.

10:40am **PS1-WeM8 Optimization of a Nitride Etch Process Using Optical Detection of NO***, F.G. Celii, **C. Huffman**,* Texas Instruments, Inc.*; J. Hosch,* Verity Instruments

With many copper backend integration schemes, silicon nitride (SiN) etch stop layers are etched over copper. Because of misalignment, the SiN etch may also occur over oxide, where high selectivity to oxide would be desired. Typical plasma conditions use fluorocarbons with O@sub 2@ or Ar at low plasma power, which avoids Cu sputtering; however, the selectivity to oxide is typically low (~2:1). Etch conditions in a remote plasma reactor have been reported which give higher nitride:oxide selectivity based on the role of NO to enhance etching of SiN.@footnote 1@ We report the use of optical emission spectroscopy to optimize NO concentration in N@sub 2@/O@sub 2@/Ar plasmas, with or without a fluorocarbon source, for use in SiN etching. Signature spectra of excited molecular (N@sub 2@*, NO*) and atomic (O*, Ar*) species were identified and tracked over various plasma conditions in a commercial etch reactor. Small corrections were made using the Ar* intensities. While the relative concentrations of N@sub 2@* and O* species are linear with N@sub 2@ and O@sub 2@ flow, the NO concentration shows a maximum which occurs at a flow ratio of ~90/10 N@sub 2@/O@sub 2@. Survey etch experiments were run with blanket oxide and nitride wafers, using conditions of maximum NO concentration.

Variation of the other process conditions showed that decreased bias power, along with increased NO and F conditions, lead to increased nitride/oxide selectivity, including values higher than the baseline process. The extension of this work to include profile and etch rate results from patterned nitride and nitride/oxide wafers will also be reported. @FootnoteText@ @footnote 1@ B. E. E. Kastenmeier, P. J. Matsuo and G. S. Oehrlein, J. Vac. Sci. Technol., A17 (1999) 3179.

11:00am **PS1-WeM9 Ultra High Selective Silicon Nitride Etching with a Downstream Remote Plasma using CF@sub 4@/O@sub 2@/CH@sub 2@F@sub 2@***, S. Halle, K. Wilson, K. Settlemyer,* IBM Microelectronics*; **H. Kimura**,* Shibaura Technology International Corp.

A silicon nitride etch process with ultra high selectivity to silicon oxide has been developed with CF@sub 4@/O@sub 2@/CH@sub 2@F@sub 2@/X , where X = Ar, N@sub 2@, or no buffer gas, using remote plasma chemical downstream etching. The application of an ion damage free, isotropic removal of a silicon nitride film over thin oxide has been limited to date due to the lack of a ultra high selective dry strip process with a high etch rate and good cross wafer uniformity. In contrast to previously reported work, the CF@sub 4@/O@sub 2@/CH@sub 2@F@sub 2@/X process achieves an oxide selectivity > 70:1, while maintaining a high silicon nitride etch rate >200 nm/min and a uniformity ~ 3% 1@sigma@. The addition of CH@sub 2@F@sub 2@ to the well characterized microwave discharge of CF@sub4@/O@sub 2@ and CF@sub 4@/O@sub 2@/CH@sub 2@F@sub 2@ is found to increase the silicon nitride etch by a factor of 4 and 2, while maintaining an oxide etch rate of approximately 60-70 and 30-40 Å/min, respectively. Although a small amount of N@sub 2@ addition to a CF@sub 4@/O@sub 2@ plasma has been shown to significantly enhance the silicon nitride etch rate, only in the regime of N@sub 2@/(N@sub 2@+O@sub 2@) > 0.4 does the etch rate linearly increase with N@sub 2@ addition. A film deposition, post etching, on the wafer surface is found to be water soluble. In addition, the silicon nitride etch rate decreases by a factor of 5 as the wafer temperatures increases from 50 to 70C. Experimental observations are consistent with a reactive surface layer mechanism, whereby an enhanced silicon nitride etch rate is achieved as the layer is thinned in the presence of nitric oxide (NO).

Plasma Science

Room 104 - Session PS2-WeM

Modeling

8:20am **PS2-WeM1 Time-Dependent Electron Impact Source Functions in Inductive and Capacitive Plasma Sources Obtained Using an "On-The-Fly" Monte-Carlo Technique@footnote 1@***, **A. Sankaran**, M.J. Kushner,* University of Illinois

Electron temperatures in low-pressure inductively and capacitively coupled plasma reactors do not significantly vary during the rf cycle. There can be, however, considerable modulation of rate coefficients and source functions for electron impact reactions having high threshold due to modulation in the tail of the electron energy distribution at energies which are less collisional. Since the character of this modulation requires that the electron energy distribution (EED) be resolved, we developed a new "On-the-Fly" (OTF) Monte-Carlo technique to compute the time dependent properties of EEDs. Using this method, Fourier frequency coefficients of the moments of the EEDs are obtained as a function of position in the reactor. The time dependence of the resulting electron impact processes are then reconstructed as a time series. The OTF method was incorporated into the Electron Monte Carlo module of a 2-dimensional plasma equipment model. The time and spatial variation of low and high threshold processes in rare gas/molecular gas mixtures will be discussed, comparing systematic trends in ICP, capacitive and helicon plasma sources. In ICPs, we found that time dependence of high threshold events such as ionization are dominated by even harmonics, whereas in asymmetric CCPs, odd harmonics are also important. The harmonic content of sources increases with increasing threshold energy and pressure. @FootnoteText@ @footnote 1@Work supported by NSF, SRC and Applied Materials

8:40am **PS2-WeM2 Global Neutral Modeling of Fluorine Plasma Etching for MEMS Applications***, **R.L. Jarecki**, M.G. Blain, R.J. Shul,* Sandia National Laboratories

The advent of time-sequenced processes featuring alternating fluorocarbon (i.e. C@sub 4@F@sub 8@) deposition and fluorine-based (i.e. SF@sub 6@) etching steps for very deep (@>=@100 µm) and mask-selective (@>=@100:1) etching of silicon@footnote 1@ has made fabrication of advanced bulk MEMS (micro-electro-mechanical systems) devices much more feasible. This intriguing new application suddenly makes the fundamental process of ion-assisted etching of silicon by atomic fluorine of much greater research interest. In this work, a simple continuous stirred tank reactor (CSTR) framework has been used to model representative neutral species in an inductively-coupled etch tool during SF@sub 6@/Ar plasma etching. The well-established technique of actinometry has been employed to assess the mean relative fluorine concentration by ratioing the F I (703.7 nm) and Ar I (750.4 nm) atomic line emission collected by an optical multichannel analyzer (OMA). A strong correlation of the pressure rise upon discharge, at fixed throttle valve position, to actinometric fluorine concentration has been observed, in agreement with the CSTR model. Silicon etch rates have also been measured. By testing a range of source powers, throttle valve positions, and flowrates, the fluorine losses for a particular reactor can be characterized to complete the CSTR model. Such a model makes possible reasonable extrapolations of fluorine concentration, and hence silicon etch rate, and can potentially speed evaluation of ultimate process limits for a given hardware configuration, as well as facilitate etch process development.@footnote 2@ @FootnoteText@ @footnote 1@U.S. Patent 5,501,893, Laermer, et al., March 26, 1996. @footnote 2@Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

9:00am **PS2-WeM3 Instabilities in Low-Pressure Electronegative Inductive Discharges***, P. Chabert,* Ecole Polytechnique, France*; A.J. Lichtenberg, **M.A. Lieberman**, A.M. Marakhtanov, H.B. Smith,* University of California, Berkeley*; M. Tuszewski,* Los Alamos National Laboratory

Plasma instabilities are sometimes seen in commercial inductive processing tools with attaching gas feedstocks. We have studied these instabilities experimentally in low-pressure inductive discharges with Ar/SF6 mixtures using optical emission, Langmuir probes, microwave diagnostics, neutral and ion mass spectrometry, a fast video camera, and voltage-current sensors. The onset of instability as a function of pressure and driving power was explored for gas pressures between 2.5 and 100 mTorr and absorbed powers between 150 and 1200 W. The frequency of the oscillations increases with pressure and lies between 1 and 100 kHz. At a given pressure, there is a power window at the transition from capacitive to inductive modes where oscillations are seen in charged particle density, electron temperature and plasma potential (the unstable region). The instability window gets smaller as the argon partial pressure increases. The settings of the matching network influence the frequency of the instability. We have improved a previously developed volume-averaged (global) model to describe the instability. We consider a cylindrical discharge containing time varying densities of electrons, positive ions, negative ions, and time invariant excited states. The driving power is applied to the discharge through a conventional L-type capacitive matching network, and we use realistic models for the inductive and capacitive energy deposition and the particle losses. The particle and energy balance equations are integrated, considering quasi-neutrality in the plasma volume and charge balance at the walls, to produce the dynamical behavior. As pressure or power is varied to cross a threshold, the instability is born at a Hopf bifurcation, with relaxation oscillations between higher and lower density states. The model qualitatively agrees with experimental observations, and phase plane portraits of the dynamics found experimentally and theoretically are in good agreement.

9:20am **PS2-WeM4 3-Dimensional Modeling of Asymmetric Gas Heating in Plasma Processing Reactors@footnote 1@***, **P. Subramonium**, M.J. Kushner,* University of Illinois

As wafer sizes increase, obtaining uniform processing conditions becomes more problematic particularly with respect to side-to-side asymmetries. Side pumping or gas injection produces asymmetries not only in the gas density but also in ion temperatures and fluxes. As a major source of gas heating is momentum transfer from ions, small asymmetries in ion temperatures are amplified through asymmetries in gas pressure. To investigate the consequences and prevalence of asymmetric gas heating and gas temperatures, a 3-dimensional plasma equipment model was improved by adding multi-fluid modules for gas and ion temperatures. A temperature is computed for each neutral and heavy particle species, while accounting for convective transport, conduction, compressive heating, sources, momentum exchange between species and temperature jumps at surfaces. As ion heating occurs dominantly in the presheath, we found that asymmetries which perturb the presheath produce gradients in ion temperature which in turn produce gas heating. Somewhat counter-intuitive, we therefore find higher gas temperatures near ports due to there being higher ion temperatures in the presheath. We will also discuss the consequences of 3-dimensional coil structures on gas heating. @FootnoteText@ @footnote 1@Work supported by NSF, SRC and Applied Materials.

9:40am **PS2-WeM5 Electron-Molecule Collisions in Processing Plasmas@footnote 1@*, V. McKoy,*** California Institute of Technology **INVITED**

In the plasmas that are widely used in semiconductor fabrication, inelastic collisions between low-energy electrons and polyatomic gases are the principal mechanism for the production of the reactive species responsible for etching and other processes at wafer surfaces. An understanding of the behavior of these plasmas thus depends on knowledge of the relevant electron-molecule collision cross sections. However, such cross sections, particularly those for the production of neutral fragments, are difficult to measure or to calculate and are often unknown for gases of interest. Over the past several years we have been exploiting large-scale parallel computers to calculate electron-collision cross sections for numerous flurocarbon feed gases and their radicals. In this talk, I will give an overview of these calculations and examples of the results we have obtained. @FootnoteText@ @footnote 1@Work supported by Sematech, Inc. and Intel Corp. and done in collaboration with Carl Winstead and M. H. F. Bettega.

10:20am **PS2-WeM7 Ionization Mechanism in ICPs*, F.F. Chen,*** UCLA

Inductively coupled plasmas with antennas wrapped around the radial surface of a cylinder are known to produce uniform plasma density profiles even though the skin depth is smaller than the discharge radius. The penetration of rf energy into interior regions has been attributed to the anomalous skin effect, in which thermal motions carry ionizing electrons past the skin layer,@footnote 1@ or to the nonlinear generation of 2nd harmonic currents.@footnote 2@ We have computed the orbits of electrons starting at arbitrary positions as they are accelerated and decelerated at different rf phases. Elastic and inelastic collisions are taken into account, and electrons are reflected when they strike the wall sheath unless they have sufficient energy to penetrate it, in which case they are lost and replaced by a slow electron elsewhere. The nonlinear Lorentz force preferentially pushes fast current-carrying electrons toward the axis. This effect, coupled with reflections from the curved wall, generates a population of fast, ionizing electrons distributed throughout the discharge. This dominant mechanism eliminates the need to place antenna elements at small radii. @FootnoteText@ @footnote 1@V.A. Godyak and V.I. Kolobov, Phys. Rev. Lett. 81, 369 (1998). @footnote 2@R.B. Piejak and V.A. Godyak, Appl. Phys. Lett. 76, 2188 (2000).

10:40am **PS2-WeM8 A 3-dimensional Model for Wave Propagation and Plasma Properties in Magnetically Enhanced ICP Reactors@footnote 1@*, R.L. Kinder*,** *M.J. Kushner,* University of Illinois

Electromagnetic wave propagation in magnetically enhanced inductively coupled plasmas (MEICPs) enables power deposition to occur remotely from the coils and at locations beyond the classical skin depth. 3-dimensional, azimuthally symmetric components of the electric field can be produced by an azimuthally symmetric (m=0) antenna in flaring solenoidal static magnetic fields. Asymmetric antennas (m=+1,-1) produce 3-d components of the electric field lacking any significant symmetries, and so must be fully resolved in 3-dimensions. To investigate these processes, a 3-dimensional plasma equipment model was improved to resolve 3-d components of the electric field produced by m=+1,-1 antennas in flaring magnetic fields. A tensor conductivity was used to couple the components while solving the wave equation in the frequency domain using an iterative, sparse matrix technique. For gas pressures of 2-20 mTorr, magnetic fields of 10-300 G, we observe rotation of the electric field downstream of the antenna where significant power deposition also occurs. Feedback from the plasma which produces local extrema in conductivity (e.g., ionization rates and electron temperatures peak where fields are largest) result in the electric field patterns not having pure modal content. Comparisons for electron density and temperature will be made to probe measurements made in a MEICP having a helicon source. @FootnoteText@ @footnote 1@Work supported by NSF, SRC and Applied Materials

11:00am **PS2-WeM9 Modeling of Fundamental Processes in a Capacitively Coupled Helium Atmospheric-Pressure Glow Discharges*, X. Yuan,*** *L.L. Raja,* Colorado School of Mines

Stable, large-volume, non-equilibrium plasmas, called Atmospheric-Pressure Glow Discharges (APGD), are emerging as an important new class of glow discharges with several potential applications in materials processing. These discharges operate in a previously inaccessible regime of the plasma parameter space, where properties resemble low-pressure glow plasmas but at significantly higher (atmospheric) pressures. Recently, several investigators have reported the generation of large-volume APGD and uses of APGD in the processing of materials. However, there exists no clear explanation of the structure of these discharges and the reasons for their stability. This paper reports detailed one-dimensional model-based investigation of a capacitively coupled APGD. The paper will discuss the structure of these highly collisional, non-equilibrium plasmas and the chemical nature of these discharges. Model predictions of the stability boundaries of the discharge will be reported. Results show that for certain operating conditions and working gas compositions, stable operating regimes between breakdown and arcing are obtained. Model predictions for discharge V-I characteristics and the stability boundaries are compared to experimental results reported in the literature. @FootnoteText@ This work is supported by a NSF-CAREER Award.

11:20am **PS2-WeM10 A Novel Approach for Control of High-Density Plasma Process Parameters through Optimal Pulse Shaping*, T.L. Vincent*,** *L.L. Raja,* Colorado School of Mines

Increasingly stringent requirements in the manufacture of Integrated Circuits (IC) are demanding new approaches for the design and operation of semiconductor process equipment and plasma process equipment in particular. Indeed, several novel plasma process techniques have been proposed recently, one of which is the operation of plasma reactors in a pulsed mode. In this approach, the main ICP power to a High-Density Plasma (HDP) reactor is deliberately modulated using square-wave pulses to provide control of plasma process characteristics. Square-wave pulsed operation has been demonstrated to improve etch/deposition rates of thin films, etch selectivity, and process uniformity. In this study, we propose a completely general technique, called "pulse shaping", for the dynamic operation of plasma reactors. Pulse shaping uses a numerical optimal control methodology for the systematic design of power modulation waveforms to achieve user-specified plasma process conditions. In the work discussed here, a time-dependent global model for an argon HDP reactor is used in conjunction with an optimal control algorithm to demonstrate that optimal design of pulse shapes can be achieved to simultaneously control time-averaged bulk plasma electron temperature and active species composition. Results are presented to illustrate the potential for significantly improved control of plasma characteristics over simple square-wave modulation of reactor power.

Surface Science
Room 122 - Session SS+SC-WeM

Adsorption on Semiconductor and Metal Oxide Surfaces

Moderator: R.J. Lad, University of Maine

8:20am **SS+SC-WeM1 Empirical Density Functionals and the Adsorption of Organic Molecules on Si(100)*, M.A. Phillips,*** *N.A. Besley, P.M.W. Gill, P. Moriarty, P.H. Beton,* The University of Nottingham, UK

Density Functional Theory (DFT) has been used in the study of the adsorption of organic molecules such as ethene and ethyne for a number of years. Typically, for semiconductor surfaces, DFT methods are used in conjunction with a cluster model of the substrate.@footnote 1@ However, the computational expense of DFT calculations implies an upper limit on the size of the substrate model, and thus on the size of adsorbate molecule. As such, the study of larger adsorbates requires some reduction in computational expense, often leading to the use of parameterised semi-empirical methods. Unfortunately, such methods do not give good agreement with experiment for many semiconducting elements: another approach is required for these materials. The Empirical Density Functional, EDF1, has been shown to give very good agreement with values of atomisation energy, ionisation potential and proton affinity for the majority of species included in the G2 experimental data set.@footnote 2@ Furthermore, this functional does not require the evaluation of 'exact exchange' contributions, and is therefore significantly less computationally expensive than 'hybrid' functionals. However, the success of EDF1 in the determination of any other physio-chemical properties, in particular adsorption geometry, adsorption energy and vibrational structure, has never been tested. Here, we present the results from a density functional study of the adsorption of organic molecules on the Si(100) surface using EDF1, and discuss their validity through comparison to experimental measurements and results from equivalent calculations using the well known functional, B3LYP. We also compare the computational expense when using EDF1 in these calculations to that when B3LYP is used. @FootnoteText@ @footnote 1@ R. Konecný and D. J. Doren, Surf. Sci. 417 (1998), 169-188. @footnote 2@ R. D. Adamson, P. M. W. Gill and J. A. Pople, Chem. Phys. Lett. 284 (1998), 6-11.

8:40am **SS+SC-WeM2 Scanning Tunneling Microscope Investigation of Adsorption of Titanium Atoms on Si(111)-7x7 Surface***, **H.F. Hsu**, M.C. Lu,* National Tsing Hua University, Taiwan, R.O.C.*; H.-L. Hsiao,* Tunghai University, Taiwan, R.O.C., Taiwan*; L.J. Chen,* National Tsing Hua University, Taiwan, R.O.C.

C54-TiSi@sub 2@ has been the primary silicide for contact application in ULSI devices. The initial stages of interfacial reactions of Ti thin films on silicon are of both scientific and the technological interests. The strong reactivity of Ti with Si was manifested by the interatomic mixing at room temperature. The atomic scale studies of initial Ti-Si reactions at very low coverage have been scarce. In particular, it is not clear whether Ti atoms react with the Si substrate from the very beginning of deposition or the formation of a silicide-like compound starts at some critical coverage. In the present study, an atomic-scale characterization of room temperature titanium adsorption on the Si(111)-7x7 surface has been investigated. Preferential adsorption of Ti atoms on the Si center adatom sites at very low coverage was found. At higher coverage, a peculiar contrast feature is observed. The observed feature is attributed to the charge redistribution caused by the adsorption of more than one Ti atoms on this subunit cell. At very low Ti coverage (~0.007 ML), some of the Si adatom sites appear to be brighter in both filled-state and empty-state STM images. The contract behavior is likely to be due to the adsorption of Ti atoms on the Si adatom sites. It was found that Ti atoms adsorb preferentially on top of the Si center adatoms and, to a less extent, on top of the Si corner adatoms. Upon further deposition of Ti, two center adatoms and corresponding corner adatom become darker and the center of these three adatoms become brighter. The observed change in the apparent height is caused by the redistribution of charge near the Si adatom sites. The result indicates that more than one Ti atoms were adsorbed on a triangular subunit cell.

9:00am **SS+SC-WeM3 High-Resolution Core-Level Study of the Initial Stage of Oxygen Adsorption on a Si(111)-(7x7) Surface***, **K. Sakamoto**, H.M. Zhang, R.I.G. Uhrberg,* Linköping University, Sweden

As motivated by the technological importance of thin silicon oxide films in semiconductor devices, the initial stage of oxygen adsorption on silicon surfaces has been a topic of experimental and theoretical investigations. Among the various reports on oxygen adsorption, Si 2p core-level studies have played crucial roles in elucidating the structures of the SiO@sub 2@/Si interfaces. However, very few Si 2p studies are available for the initial stage of oxygen adsorption on a Si(111)-(7x7) surface. In this paper, we present a high-resolution Si 2p core-level photoemission study of submonolayer oxygen adsorption on the (7x7) surface. The photoemission measurements were performed at beamline 311 at the MAX-II synchrotron radiation facility in Lund, Sweden. The clean (7x7) surface was exposed to 0.1-20 L of oxygen at 120 K, which correspond to coverages below 1 ML. Significant intensity of the Si 2p component due to the Si@super 2+@ species is observed already at 0.3 L, and the component due to the Si@super 3+@ species is clearly observed at a dosage higher than 1.0 L. These results indicate that more than two oxygen atoms adsorb to one Si atom even at a very low coverage. After annealing the oxygen adsorbed sample at 600 K, the Si 2p component due to the Si@super 2+@ species shows a shift of 0.4 eV to the higher binding energy side. This result suggests different atomic configurations for the Si@super 2+@ species at 120 K and after annealing the sample at 600 K. We will also present detailed studies of the dosage- and temperature-dependent intensities of the Si 2p components due to the suboxide species.

9:20am **SS+SC-WeM4 First-Principles Theory of Finite-Temperature Adsorbate Ordering in Ba/Si(111)-"3x2"***, **S.C. Erwin**, C.S. Hellberg,* Naval Research Laboratory

Alkali metal adsorbates induce a 3x1 reconstruction of Si(111) widely believed to be a "honeycomb-chain channel" structure. This model is based on a true Si=Si double bond in the surface layer, which at 1/3 ML coverage leads to the elimination of all dangling bonds and thus keeps the fundamental gap free of surface states. Alkaline-earth adsorbates also appear to induce 3x1 (as well as higher-order) reconstructions, yet despite the extra electron the resulting surfaces remain fully gapped---an apparent contradiction to the one-electron band picture. Lee et al. recently suggested that for alkaline-earth adsorbates the coverage is in fact 1/6 ML, and showed that a 3x2 honeycomb-chain channel model is indeed fully gapped.@footnte 1@ We use density-functional methods first to confirm that the model of Lee et al. is indeed energetically preferred at low coverages. Second, we predict that structurally related 5x2 and 2x1 reconstructions will appear---if they are not preempted---at higher coverages. Finally, we propose an explanation for why the 1/6 ML phase appears 3x2 in STM but 3x1 in LEED: namely, that at moderate temperatures the adsorbates will exhibit only short-range order, due the near energetic degeneracy of H3 and T4 adsorption sites. To demonstrate this, we extract from our density-functional calculations the adsorbate-substrate and adsorbate-adsorbate interactions, and based on these carry out classical Monte Carlo simulations to explore the detailed temperature dependence of adsorbate ordering. @FootnoteText@@footnte 1@G. Lee, D. Shin, H. Kim, J. Koo, and S. Hong, Bull. Amer. Phys. Soc. 46 (2001).

10:00am **SS+SC-WeM6 Adsorption Induced Deflection and Frequency Changes in a Silicon Nitride Cantilever due to Ca@super 2+@ Ions***, **S. Cherian**, A. Mehta, T.G. Thundat,* Oak Ridge National Laboratory

Cantilever based micromechanical sensors exploit changes in surface stress due to interactions between the analyte species and cantilever surface. Charged groups on the cantilever surface play a significant role in binding induced deflection of the micro-cantilever. The deflection and frequency response of triangular silicon nitride cantilevers when exposed to calcium chloride solution was investigated in a flow system. The silicon nitride cantilever used was 200µm long and 20µm wide. Calcium chloride solutions of increasing concentrations were injected sequentially into the flow cell and the cantilever response measured. The fundamental resonance frequency of the cantilever shifted to lower values with increasing solution concentrations. The deflections due to interaction with the CaCl@sub 2@ were towards the gold side. The concentration versus deflection curve followed a Langmuir adsorption isotherm. The cantilever response is attributed to chemisorption of calcium ions onto the silicon nitride side. To verify this a calcium binding protein, calmodulin, was used. A cantilever that was exposed to CaCl@sub 2@ solution was subsequently exposed to calmodulin. Calmodulin binding to Ca @super 2+@ ions on the cantilever surface resulted in a deflection. This deflection was significantly different from that observed when calmodulin was exposed onto a fresh cantilever. These observations were further confirmed by fluorescent measurements using a fluorescently tagged calmodulin. These results demonstrate that consideration of ionic interactions of charged species in the medium with cantilever surfaces is critical in interpreting deflection data of cantilever based sensors. This also suggests the importance of passivating one of the surfaces in order to make the deflection of the functionalized cantilever specific to the species of interest.

10:20am **SS+SC-WeM7 Adsorption of NO and NO@sub 2@ on Barium Oxide: Surface Nitrition and Nitration***, P.J. Schmitz, R.J. Baird,* Ford Motor Company*; **M. Miletic**, J.L. Gland,* University of Michigan

Alkaline earth oxides surfaces are known to trap NOx species by chemisorption even under excess oxygen conditions typical of lean burn engines exhaust. These oxides, particularly barium oxide, have been proposed as active components in cyclic automotive NOx abatement strategies because of their ability to store and release NOx under rich/lean exhaust cycling. However, molecular understanding of the adsorption and reactions of NO, and NO2 on alkaline earth oxide surfaces remains incomplete. A series of XPS and temperature programmed studies of NO and NO2 adsorption and reaction on model barium oxide thin films prepared in-situ are reported here. These experiments indicate that charge transfer and reactive chemisorption play an important role even during low temperature adsorption on barium oxide surfaces. Nitrite and nitrate species form preferentially on reactive adsorption sites and can be reactively desorbed in the 400 to 600 K temperature range. The coverage of the precursor molecular species plays an unexpected role both in reactive adsorption and desorption on barium oxide surfaces. These results are discussed in terms of recent DFT calculations which highlight the importance of reactive configurations, charge transfer, and surface oxidation/reduction processes.

10:40am **SS+SC-WeM8 Electronegative Adsorbates on TiO@sub 2@: Reducing Effects of S and Cl**, ***E.L.D. Hebenstreit***[1], *W. Hebenstreit,* Tulane University*; H. Geisler,* Xavier University of Louisiana*; C.A. Ventrice, Jr.,* University of New Orleans*; D.A. Hite, P.T. Sprunger,* Louisiana State University*; U. Diebold,* Tulane University

TiO@sub 2@(110) is a well-studied model catalyst with an abundance of technical applications. Sulfur and chlorine are common impurities in many catalytic systems which poison catalytic reactions. The adsorption of molecular S and Cl on TiO@sub 2@(110)(1 x 1) has been studied with scanning tunneling microscopy (STM), x-ray and ultraviolet photoelectron spectroscopy (XPS, UPS), and low energy electron diffraction (LEED). At room temperature both adsorbates bind dissociatively to 5-fold coordinated Ti atoms and oxygen vacancies. At elevated temperatures (120°C - 440°C), S and Cl replace surface oxygen atoms. S forms different types of superstructures in dependence on coverage and adsorption temperature. No long-range ordering was found in the a dsorbed layer for Cl. Both adsorbates reduce the surface but S leads to a stronger oxygen depletion than Cl. In photoemission experiments, adsorption of either S or Cl at elevated temperatures cause additional emission at the high binding energy side of t he valence band and increases emission from the defect state. Adsorption of S leads to band gap states which fill the band gap completely. Evidence was found that the reduction state of TiO@sub 2@ crystals strongly affects the surface coverage of S and Cl at elevated temperatures. The rate of the site exchange of the adsobates between a weakly bound precursor state on Ti and the replacement of oxygen is kinetically limited by the arrival of diffusing bulk defects at the surface.

11:00am **SS+SC-WeM9 Electronic and Chemical Properties of Ce@sub 0.8@Zr@sub 0.2@O@sub 2@(111) Surfaces: Photoemission, XANES, Density Functional, and NO@sub 2@ Adsorption Studies**, ***G. Liu***, *J.A. Rodriguez, J. Hrbek, J. Dvorak,* Brookhaven National Laboratory*; C.H.F. Peden,* Pacific Northwest National Laboratory

Synchrotron-based photoemission,conventional XPS, XANES, and first-principles density functional (DF) calculations were used to study the electronic properties of a Ce@sub 0.8@Zr@sub 0.2@O@sub 2@ mixed-metal oxide. The results of DF calculations show that the band gap in bulk Ce@sub 0.8@Zr@sub 0.2@O@sub 2@ is ~ 0.6 eV smaller than in bulk CeO@sub 2@, with the Zr atoms in the mixed-metal oxide showing smaller positive charges than the cations in ZrO@sub 2@ or CeO@sub 2@. When present in a lattice of CeO@sub 2@, the Zr atoms are forced to adopt larger metal-O distances than in ZrO@sub 2@, leading to a reduction in the oxidation state of this element. Due to non-equivalent Zr-O distances, at least three different types of oxygen atoms are found in the Ce@sub 0.8@Zr@sub 0.2@O@sub 2@ system. O K-edge XANES spectra for a series of Ce@sub 1-x@Zr@sub x@O@sub 2@ (x=0, 0.1, 0.2, 0.3, 1) compounds show a distinctive line shape for the mixed-metal oxides that can not be attributed to a sum of CeO@sub 2@ and ZrO@sub 2@ features, supporting the idea that the O atoms in Ce@sub 1-x@Zr@sub x@O@sub 2@ are in a special chemical environment. XPS Ce 3d spectra show the presence of Ce@super 3+@ cations which may be related to the relative stability of oxygen vacancy defects upon incorporation of zirconia into ceria. The interaction of NO@sub 2@ gas with Ce@sub 0.8@Zr@sub 0.2@O@sub 2-x@(111), CeO@sub 2-x@(111), and Zr(Y)O@sub 2-x@(111) reduced surfaces was examined. Ne@super +@ ion sputtering was used to generate substantial concentrations of Ce@super 3+@, Zr@super 2+@ and Zr0 centers on the oxide surfaces. On CeO@sub 2-x@(111), NO@sub 3@, NO@sub 2@ and N were seen upon adsorption of NO@sub 2@. In contrast, only NO@sub 2@ and N were detected after adsorption of NO@sub 2@ on Ce@sub 0.8@Zr@sub 0.2@O@sub 2-x@(111) and Zr(Y)O@sub 2-x@(111). Adsorption of NO@sub 2@ induced an increase in the oxidation state of the metal cations (Ce@super 3+@ to Ce@super 4+@; Zr0 to Zr@super 2+@).

11:20am **SS+SC-WeM10 Probing Chemical and Topological Heterogeneity of Carbonaceous Surfaces via Temperature Programmed Desorption of Simple Molecules from Model Carbonaceous Surfaces**, ***J. Kwon***, *R. Vidic, E. Borguet,* University of Pittsburgh

Carbonaceous surfaces find applications in fields ranging from tribology to environmental remediation to catalysis. These surfaces are generally characterized by varying extent of chemical and topological heterogeneity that affects key elementary processe s such as adsorption and desorption. Temperature programmed desorption of model adsorbents (propane and acetone), representative of polar and non-polar organic compounds, was used to investigate the role of surface chemical and topological heterogeneity on the physical and chemical properties of model carbonaceous surfaces (air cleaved and plasma oxidized highly oriented pyrolytic graphite - HOPG). We observed that hydrogen and oxygen containing functional groups, which tend to block available adsorption sites, exist on air cleaved and plasma oxidized HOPG. Thermal treatment leads to removal of these groups and to over an order of magnitude increase in adsorption capacity. Thermal treatment (> 900 oC) of carbonaceous surfaces appears essential for maximum accessibility to adsorption sites. The surface defects induced by plasma oxidation yield greater surface area available for adsorption and higher energy sites. This novel approach promises a better understanding of chemically and topologically heterogeneous nanoporous carbons used in practical applications.

Surface Science

Room 120 - Session SS1-WeM

Surface Diffusion

Moderator: G.L. Kellogg, Sandia National Laboratories

8:20am **SS1-WeM1 Diffusion on and in Surfaces: The Atomic Slide Puzzle**, ***J.W.M. Frenken***, *R. Van Gastel, E. Somfai, S.B. Van Albada, W. Van Saarloos,* Leiden University, The Netherlands **INVITED**

Usually, surface mobility is thought to be restricted completely to the steps and kinks on crystal surfaces. These sites form the natural locations for atoms to come and go. Atoms in the close-packed terraces are often considered to be completely static, since they are tightly packed by their neighbors. In this talk, measurements will be shown that have been obtained with the scanning tunneling microscope, that show that a close-packed terrace of a metal surface can be far from static, even at temperatures as low as room temperature! We make the motion visible of the atoms in a Cu(001) terrace, by embedding a low density of In atoms in the first Cu layer. The peculiar characteristics of the motion of the In show that the diffusion of surface vacancies is responsible for a continual reshuffling of all the (In and Cu) atoms in the first layer.@footnote 1@,@footnote 2@ @FootnoteText@ @footnote 1@ R. van Gastel, E. Somfai, W. van Saarloos and J.W.M. Frenken, Nature 408 (2001) 665. @footnote 2@ R. van Gastel, E. Somfai, S.B. van Albada, W. van Saarloos and J.W.M. Frenken, Phys.Rev.Lett. 86 (2001) 1562.

9:00am **SS1-WeM3 Nothing Moves a Surface: Probing Surface Vacancy Dynamics with a Surface Alloy**, ***R. Van Gastel***, *E. Somfai, S.B. Van Albada, W. Van Saarloos, J.W.M. Frenken,* Universiteit Leiden, The Netherlands

Indium atoms that are deposited on the Cu(001) surface at room temperature rapidly diffuse to steps where they are incorporated into the first layer of the crystal surface. We use the In/Cu(001) surface alloy to probe the dynamics of surface vacancies. The motion of embedded indium atoms enables us to use these atoms as `tracer' particles for the direct visualization of vacancy mediated diffusion of surface atoms.@footnote 1@ Steps on the surface act as sources and sinks for surface vacancies. This crucial role of steps is exposed as the mobility of embedded indium atoms is spatially mapped out. The temperature dependence of the diffusion of embedded indium atoms is investigated through high speed STM movies. The temperature dependence provides us with a direct measurement of the surface vacancy mobility, and yields the sum of the vacancy formation and migration energies. In addition to this, we present first results from experiments, in which monatomic surface vacancies are artificially created. From these the vacancy migration energy can be obtained so that we can experimentally separate out the formation and migration energies. @FootnoteText@ @footnote 1@R. van Gastel et al., Phys. Rev. Lett. 86 (2001), 1562.

9:20am **SS1-WeM4 Surface-diffusion Mechanism vs. Electric Field: Pt/Pt(001)***, ***P.J. Feibelman***, Sandia National Laboratories

Identifying macroscopic variables that affect the rates and mechanisms by which surface atoms move should enhance our ability to control surface morphology. The search for new "knobs to turn" is at the root of the decade-long effort to modify thin-film growth by depositing appropriately chosen "surfactant" species. It also motivates the work reported here, in which ab-initio total energy calculations are used to understand how an externally imposed electric field should affect the mechanism and rate of adatom self-diffusion on Pt(001), a surface for which Field Ion Microscopy experiments@footnote 1@ suggest that the low energy process, concerted substitution, is supplanted by hopping when the external field is high enough. The result is that theory agrees with FIM that the barrier to

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[1] **Morton S. Traum Award Finalist**

concerted substitutional diffusion of a Pt atom on Pt(001) varies linearly with external electric field (slope ~0.1eÅ), increasing for fields oriented to push electrons into the surface. But, with a computed hopping barrier remaining >0.5 eV higher than that for substitution, the calculations contradict the idea that a change in FIM site visitation at fields of 1.5-2 V/Å and temperatures ~265-284K can be attributed to the onset of hopping. @FootnoteText@ @footnote *@Work supported by the U. S. Department of Energy under Contract No. DE-AC04-94AL85000. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the U. S. Department of Energy. @footnote 1@G. L. Kellogg, Phys. Rev. Lett. 70, 1631(1993).

9:40am **SS1-WeM5 Temperature-Dependent Surface Diffusion Parameters on Amorphous Materials***, **E.G. Seebauer**, D. Llera-Hurlburt, A. Dalton,* University of Illinois, Urbana

Diffusion on amorphous surfaces represents a little-studied physical phenomenon that controls several important kinds of material processing. To elucidate some general features of this phenomenon, we have determined Arrhenius parameters for the surface self-diffusion of amorphous silicon (a-Si) by measuring the formation kinetics of hemispherical grained silicon. The results exhibit significant temperature dependence in the activation energy for total mass transport. We develop a physical model and associated mathematical formalism to show that this behavior should characterize diffusion on amorphous surfaces in general. Adatom formation on amorphous surface can arise from a near-continuum of structures and energy states. The formation energy for mobile atoms is therefore described by a continuous distribution function f(E). The breadth of f(E) on a-Si and related surfaces contrasts sharply with the sum of delta functions corresponding to kinks, steps and terraces on crystalline surfaces. Thus as T increases on amorphous surfaces, the average formation energy for mobile adatoms increases continuously, and the Arrhenius plot for total mass transport bends upward. The sharpness of the curvature depends upon the breadth of f(E); a broader distribution yields more gentle curvature.

10:00am **SS1-WeM6 Hopping Induced by the Vibrational Excitation of Adsorbed Molecule through Inelastically Tunneled Electrons***, **M. Kawai**, T. Komeda, Y. Kim,* RIKEN, Japan

There is a rising interest for the phenomena caused by inelastic tunneling in the experiments using scanning tunneling microscope (STM).@footnote 1@ In this report, we show surface-diffusion of adsorbate is induced by inelastic tunneling of electron for the molecules of CO and ethylene on Pd(110) at 4.8K. When a certain amount of tunneling electron is dosed on a single adsorbate, the change of their bonding site along [1 0] direction is observed. We study this phenomenon systematically and found that the diffusion probability shows a very sharp increase at the bias voltage of 250 mV, which corresponds to the excitation of CO stretch vibrational mode. In similar manner, ethylene molecule adsorbed on the same surface is also enhanced to hop to the neighboring sites by irradiating electrons that correspond to the excitation of the internal stretching modes. These clearly demonstrate that the vibrational mode excited by inelastically tunneled electrons opens a route to induce hopping of the adsorbed molecules on surfaces. In the case of CO on Pd(110), thermal diffusion of CO was previously studied. At 100 K, one-dimensional CO arrays are formed and attaching and detaching of CO molecules are observed. The motion is restricted on [1 0] direction. The estimated diffusion barrier for a CO molecule in an array is ~180 meV, but the value for an isolated molecule should be much smaller in energy. Here we propose a model that the diffusion of CO is induced by an excitation of high lying vibrational mode (C-O stretch mode) which is further coupled with T-mode and R-mode through anharmonic coupling to induce surface diffusion . @FootnoteText@ @footnote 1@J.R. Hahn, H.J. Lee, and W. Ho, Phys. Rev. Lett. 85 1914 (2000) and references there in.

10:20am **SS1-WeM7 Determination of Atomic Potential Energy for Pd Adatom Diffusion Across the W (111) Islands and Surfaces***, **T.-Y. Fu**,* National Taiwan Normal University, R.O.C., R. O. C.*; L.-C. Cheng,* National Taiwan Normal University, R.O.C.*; T.T. Tsong,* Academia Sinica, Taiwan, R.O.C.

Using field ion microscopy (FIM), we have probed the diffusion behavior of Pd adatoms on W (111) surfaces and in the vicinity of surface steps. From the behavior of an adatom approaching the step from the upper terrace, we find the step to be reflective to Pd adatoms. The extra reflective barrier is determined to be 0.64±0.03 eV. The behavior of adatoms approaching the step from the lower terraces has also been studied. The activation energy for the step-up motion of Pd atoms of W (111) steps is 1.84 eV. The potential energy difference toward and away from the W (111) pole exhibits a free energy anisotropy of 0.013 eV. These experimental results of atomic processes are related to the phenomenon of impurity induced pyramidal facet formation.

11:00am **SS1-WeM9 Surface Dynamics During Etching of GaAs(001)***, **S.W. Robey**,* National Institute of Standards and Technology

We present results from an experimental investigation of the surface dynamics controlling morphology during CH@sub 4@/H@sub 2@ plasma and wet etching of GaAs (001) surfaces. In the case of plasma etching, height-difference correlation functions (extracted from AFM data) indicate that morphology development is dominated by diffusion below ~ 100 nm, while desorption/etching effects dominate on larger length scales. The crossover between these two regimes is temperature dependent. Below 600 K, oscillatory structure in the height correlation function, associated with a "rippled" surface morphology, arises due to an instability in the etching dynamics. We attribute this instability to Ehrlich- Schwoebel step-edge barriers. The behavior of the height-difference correlation function and the time-dependent roughening is found to be in good agreement with studies of continuum models based on the Kuramoto-Sivashinsky (KS) equation. However, the Laplacian term in the KS equation has components arising from both the ES barrier and etching/desorption effects so that the effect of the ES barrier in producing the instability is weakened, compared to thin film growth examples. Using theoretical expressions for the kinetic coefficients in the KS equation, we find that the Ehrlich-Schwoebel barrier is ~ 0.05 eV in this system. We will also present initial results studying "facetting" during wet etching of GaAs (001). The initial formation of anisotropic "hillock" structures develops in time to form a hill-and-valley structure along the (110) direction, with faces close to [111]. The length scale coarsens in time and is dependent on the etchant composition. Comparisons with theoretical studies of kinetically controlled crystal growth and etching will be discussed.

11:20am **SS1-WeM10 Step Motion on the Cu(100)-(@sr@2x2@sr@2)R45°-O Surface***, C.L.H. Devlin,* Air Force Research Lab, U.S.*; J.P. Landry,* University of California, Davis*; N.C. Bartelt,* Sandia National Laboratories*; **S. Chiang**,* University of California, Davis

Low energy electron microscopy (LEEM) was used to study the motion of single-atom-high steps on a Cu(100) surface covered with the (@sr@2x2@sr@2)R45°-O structure. Curved steps exhibited capillary wave motion, which was analyzed using Langevin Dynamics.@footnote 1@ From this analysis, the dominant mode of adatom diffusion (i.e., along steps or over terraces) was deduced. Parameters such as the step stiffness and kink activation energy were also discovered. @FootnoteText@ @footnote 1@ N.C. Bartelt and R.M. Tromp, Phys Rev B 54 (1996) 11731.

Surface Science

Room 121 - Session SS2-WeM

Surface Reactions on Metals

Moderator: D.R. Mullins, Oak Ridge National Laboratory

8:20am **SS2-WeM1 CO Oxidation on Au Crystals: Studies on the Nanoscale***, T. Bär, T. Visart de Bocarmé,* Free University of Brussels, Belgium*; B.E. Nieuwenhuys,* Leiden University, The Netherlands*; **N. Kruse**,* Free University of Brussels, Belgium

Until recently gold was regarded as a metal of little interest for applications in heterogeneous catalysis. The discovery that supported gold catalysts are among the most active ones in CO oxidation has completely changed this picture. The mechanism of the reaction is, however, still under debate. In particular, the question for the role of the support material and for possible impurity effects must be asked. With this background we have studied oxygen activation and reaction with CO on pure Au single crystal specimens, in the absence of any oxidic support material, using Field Ion Microscopy (FIM) and atom-probe techniques. FIM-images (using H@sub 2@ and Ne as imaging gas at 55 K and at field strengths of up to 35 V/nm) indicated clean, nearly hemispherically shaped Au crystals of (111) orientation. Exposure of such a specimen to O@sub 2@ gas at 100 mbar and temperatures between 300 and 450 K, in the absence of an electric field, led to oxygen chemisorption and formation of a "surface oxide". In particular, layer edges of (111) and (100) planes were decorated by oxygen atoms. In situ studies of surface oxide formation performed in an O@sub 2@ gas atmosphere of 1,0*10@super -4@ mbar showed that the presence of an electric field of 12-15 V/nm significantly enhances oxygen adsorption. Exposure to CO gas at 300 K led to the removal of the surface oxide, i.e.

CO@sub 2@ formation. This was associated with the occurrence of a reaction front which started in the apex centre, i.e. the (111) pole, and extended in nearly concentric circles to the outskirts of the Au specimen. Using video-FIM several cycles of oxide build-up and titration with carbon monoxide were performed to demonstrate the reversibility of the surface processes. Using atom-probe techniques during the ongoing reaction AuO and AuCO ionic species could be observed in variable amounts. We conclude that pure gold crystals are active catalysts for the CO oxidation at 300 K.

8:40am **SS2-WeM2 Surface Phase Transitions of Pt(110) Studied by Desorption Dynamics of Product CO@sub 2@ in Steady-state CO Oxidation***, **I. Rzeznicka**, M.G. Moula, T. Matsushima,* Hokkaido University, Japan

This paper reports the first confirmation of the transition from (1x2) to (1x1) through angular distribution analysis of desorbing product CO@sub 2@. Clear distribution changes were observed in the inhibited region where CO retards its oxidation. The surface phase transition of Pt(110)from (1x1)to(1x2) yields differently-oriented adsorption sites of oxygen. The CO oxidation on these sites induces differently-collimated CO@sub 2@ desorption, since this desorption mostly collimates along the local normal of the site. Both the angular and velocity distributions of desorbing CO@sub 2@ will switch sharply around the transition condition. This phenomenon was examined in steady-state CO oxidation on Pt(110) in a wide range of surface temperature and reactant pressures by means of cross-correlation time-of-flight techniques. In the active region where the surface is covered by O(a), desorbing CO@sub 2@ mostly collimated in a two-directional way along +25° or -25° off the surface normal in the (001) plane. This indicates CO@sub 2@ formation on the declining (111) terraces of the (1x2) form. On the other hand, in the inhibited region where the surface is mostly covered by CO(a), the normally directed desorption was sharply enhanced at a critical CO pressure where the two-directional components were suppressed. Below 3x10@super -4@ Torr of fixed O@sub 2@, this critical pressure shifted from the kinetic transition pressure (where the inhibition by CO starts) to higher values with increasing surface temperature. This critical point was confirmed to indicate the completion of the phase transition from LEED and CO adsorption measurements.

9:00am **SS2-WeM3 Dynamic Spatial Patterns in a Surface Reaction - The Microscopic and Mesoscopic Scales***, **J. Wintterlin**, C. Sachs, M. Hildebrand, S. Voelkening, G. Ertl,* Fritz-Haber-Institut, Germany **INVITED**

One of the most spectacular observations in surface catalytic reactions is the formation of dynamic spatial patterns that are connected with non-linear terms in the reaction kinetics. We have investigated such phenomena, both on the atomic and the mesoscopic scales, for the catalytic water formation from adsorbed oxygen and hydrogen on a Pt(111) surface. By means of scanning tunneling microscopy (STM) propagating reaction fronts were observed on a 10 to 1000 nm scale. Simulations were performed with a reaction diffusion model that contains an autocatalytic reaction sequence. The model predicts reaction fronts, formed by travelling interfaces between adsorbed oxygen and water. The fronts contain the reaction intermediate OH, in full qualitative agreement with the experiment. However, quantitative simulations reveal deviations from the experiment, demonstrating the limitations of this description. The atomic scale processes in the fronts, which were resolved by STM, indicate that the reasons for these deviations lie in the simplifications of standard reaction-diffusion models, namely the assumptions of a random occupation of adsorption sites and of spatially independent kinetic constants.

9:40am **SS2-WeM5 Hydrogenation of Oxygen on Pd(111)***, **T. Mitsui**,* Lawrence Berkeley National Laboratory*; M.K. Rose, E. Fomine,* University of California, Berkeley*; F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory

The reaction of hydrogen with (2x2) oxygen islands on Pd(111) has been studied with scanning tunneling microscopy under UHV conditions. Hydrogenation of oxygen, to form OH, was observed at 25 K. The reaction destabilizes the (2x2) ordering of oxygen and results in the formation of new (@sr@3x@sr@3) islands above 120 K. The OH islands remain stable up to 210 K even after the H@sub 2@ gas phase has been removed. Above this temperature, however the OH species decompose back to oxygen which reorganizes into (2x2) structures. The (@sr@3x@sr@3) OH islands can be formed again by additional hydrogen. If H@sub 2@ gas phase (10@super -8@ torr) is maintained during heating at 220 K, the (2x2) oxygen islands disappear completely from the surface by forming of H@sub 2@O that desorbs. Based on these results, the mechanisms of the formation of H@sub 2@O on Pd(111) from oxygen and hydrogen will be discussed.

10:00am **SS2-WeM6 Abstraction of Si and SiH@sub x@ (x=1,2,3) Adsorbed on Cu(100) Surfaces with Gaseous D towards Silane***, **D. Kolovos-Vellianitis**,* EPIII, University of Bayreuth, Germany*; Th. Kammler,* Focus GmbH, Germany*; Th. Zecho, J. Kueppers,* University of Bayreuth, Germany

The study of metal-silicide interfaces is of significant imterest because of their important technological applications. In particular, a better understanding of the formation of silicon structures on metal surfaces using chemical vapor deposition (CVD) of silane and disilane can provide valuable information about the elementary processes of adsorption, dissociation and reaction with other gaseous atoms. The interaction of silane and disilane with Cu(100) surfaces was studied in the temperature range 77 K to 650 K with thermal desorption and Auger electron spectroscopies. Silane admission to Cu(100) at low temperatures initially leads to a complete decomposition of the silanes into adsorbed Si and H. Close to saturation of the surface with H, SiH@sub x@ species remain intact on the surface. They were identified as SiH@sub 3@ and to a smaller extent SiH@sub 2@ by monitoring the silane abstraction products and their kinetics during admitting gaseous D to the surface between 77 K and 200 K. Silane desorption through recombination of SiH@sub 3@ and SiH@sub 2@ with adsorbed H occurs around 157 K and 224 K, respectively. After hydrogen desorption around 300 K a Si covered surface remains, which can be converted to a clean Cu(100) surface by activating Si bulk diffusion around 700 K. Adsorbed Si is abstracted from the surface below 200 K by gaseous H via formation of silane through a sequence of 4 hydrogenation steps. The first hydrogenation reaction is rate determining and is significantly accelerated by increasing the temperature between 77 K and 200 K. Above 200 K a thermally unstable SiH@sub x@ species blocks the abstraction reaction. The reaction kinetics phenomenology is in accordance with an Eley-Rideal scenario.

10:20am **SS2-WeM7 Catalytic Reactions on Alkali-modified Vicinal Cu(100) Surfaces***, **J Onsgaard**,* Aalborg University, Denmark*; J.P. Godowski,* University of Wroclaw, Poland*; S.V. Hoffmann,* Aarhus University, Denmark*; L. Bech,* Odense University, Denmark

Coadsorption of atoms and molecules with alkali-metal(AM) atoms on single crystal metal surfaces is of importance in heterogenous catalysis. The roles of AM (K or Cs) coverage and steps on vicinal Cu(100) surfaces - Cu(115) and Cu(117) - have been studied with respect to reactivity with low-molecular gases. It is demonstrated that the presence of steps and AM in the submonolayer coverage regime enhances the reactive properties of these surfaces. The Cu(115) surface, particularly, but also the Cu(117) surface modified with AM exhibit a high surface reactivity. The processes studied include dissociation of CO and synthesis of formate from coadsorption of H and CO@sub 2@. The C and O 1s core level shifts and the changes in the intensities of the satellite peaks are discussed in terms of the CO-substrate and/or the interatomic C-O interactions. A series of techniques, including photoelectron spectroscopy based on synchrotron radiation, thermally programmed desorption, work function measurements and LEED has been used.

11:00am **SS2-WeM9 Formation of Methylaminomethylidyne(>CNH(CH@sub 3@)) by Hydrogenation of Methyl Isocyanide and by Dehydrogenation of Dimethylamine on Pt(111)***, **D.H. Kang**, M.W, Trenary,* University of Illinois at Chicago

Fourier transform-reflection absorption infrared spectroscopy(FT-RAIRS) and temperature programmed desorption (TPD) have been used to study the adsorption and the surface reaction of methyl isocyanide (CNCH@sub3@) and dimethylamine ((CH@sub3@)@sub2@NH)) on the Pt(111)surface. Our previous studies have shown that the CN containing molecules, like azomethane (CH@sub3@N=NCH@sub3@), methylamine (CH@sub3@NH@sub2@) and hydrogen cyanide (HCN), have a common highly stable intermediate, aminomethylidyne (>CNH@sub2@), which is an aminocarbyne (>CNR@aa R@) species. An aminocarbyne species is a likely surface intermediate that could be formed by hydrogenation of the isocyanides and by dehydrogenation of amines.It is, therefore, of great interest to understand the adsorption and surface reaction of isocyanides and amines on metal surfaces. At low coverage and 85 K, methyl isocyanide adsorbs at on-top sites with an upright structure and then adsorbs on bridge sites at higher coverage. The RAIR spectra show new peaks by exposing hydrogen to the sample at or above 200 K, indicating a new surface species formed by hydrogenation. This species is identified as methylaminomethylidyne (MAM),(>CNH(CH@sub3@)),and exists as a stable species up to 350 K. Dimethylamine (DMA) adsorbs molecularly at 85K and the RAIR spectra show the same characteristic peaks as the hydrogenation of methyl isocyanide after annealing the sample to 350 K. This MAM species could be formed by the dehydrogenation of DMA as shown by TPD. At 400 K, the MAM species changes to a (>CNCH@sub3@) species, by dehydrogenation of the N-H bond and part of the (>CNCH@sub3@) species rearranges to the on-top site methyl isocyanide. When coadsorbing hydrogen at 300 K following annealing the sample to 400 K, part of the (>CNCH@sub3@) species changes to MAM by hydrogenation. The RAIR spectra also show peaks corresponding to aminomethylidyne (>CNH@sub2@), suggesting the existence of CN on the surface at 400 K.

11:20am **SS2-WeM10 Experimental and Theoretical Imaging of the Decomposition of Furan on Pd(111)***, **A. Loui,*** University of California, Davis*; D.N. Futaba,* Hokkaido University, Japan*; S. Chiang,* University of California, Davis

Experimental and theoretical studies have been performed on the decomposition of furan, C@sub4@H@sub4@O, adsorbed on Pd(111). The reaction of furan on this substrate has been previously studied using LITD/FTMS.@footnote 1@ In that study, furan was observed to decompose to H, CO, and C@sub3@H@sub3@ in the temperature range of 280-320 K; the latter species can then dimerize to form benzene above 350 K. Using scanning tunneling microscopy, our observations of the pre-reaction surface at 126 K show features adsorbed along the upper step edges, which match theoretical images of furan@footnote 2@ (generated using Extended Hückel Theory) in overall shape, size and internal structure. Comparison of the calculated and experimental furan features show that these molecules seem to preferentially orient with the oxygen atom facing away from or towards the step edge. Data obtained in the temperature range of 280-320 K show evidence of decomposition, which is consistent with the previous desorption studies. We have observed two distinct types of features that are discernible based on size, location and internal detail. The larger features populate the upper step edge region and are consistent with the data obtained at 126 K for unreacted furan. The smaller features appear to be clumped along the lower step edges. Based on the size and the known reaction products, we attribute these features to C@sub3@H@sub3@. In some reaction data, this species is resolved as an oblong feature with a bisecting node, agreeing well with the calculated images for flat-lying C@sub3@H@sub3@ molecules in shape, size and internal structure. These experiments indicate that there is a fundamental difference in the properties of the upper step edge versus the terrace with respect to this decomposition reaction. @FootnoteText@ @footnote 1@ Caldwell, T. E. and Land, D. P., Polyhedron, 16(18), 3197 (1997). @footnote 2@ Futaba, D. N. and Chiang, S., J. Vac. Sci. Technol. A, 15(3), 1295 (1997).

Thin Films
Room 123 - Session TF-WeM
Fundamentals of Deposition

Moderator: J. Colligon, Manchester Metropolitan University, U.K.

8:40am **TF-WeM2 Molecular Dynamics Simulations of Self-bombardment of Compact Clusters on Pt(111)***, **D. Adamovic**, E.P. Münger, V. Chirita, L. Hultman,* Linköping University, Sweden*; J.E. Greene,* University of Illinois, Urbana

Studies of low-energy bombardment of two-dimensional (2D) close-packed clusters are of great importance and strongly related to thin film growth. We use embedded-atom method molecular dynamics simulations to monitor the kinetics characterizing the self-bombardment of Pt@sub 3@, Pt@sub 7@ and Pt@sub 19@ clusters on Pt(111) at 1000K. Atoms incident perpendicular to the surface with energies between 5 and 50 eV are followed in separate simulations of ~ 20 ps each. Clusters are divided into different sections, outer, rim and core area respectively. Our simulations reveal three major classes of events. They are cluster preservation, i.e. no change in shape or position, cluster reconfiguration, involving edge-diffusion and/or concerted dimer/trimer gliding and cluster disruption (rim atom scattering and/or total disintegration). Two of the most commonly observed events are the formation of three-dimensional (3D) clusters and the hopping and/or push out/exchange mechanism with rim atoms. Other typical processes observed are the permanent or temporary dislodgement of cluster atoms onto the surface as well as the creation of surface vacancies. For Pt@sub 3@ our results suggest that cluster preservation and reconfiguration events primarily occur with incident atom energies below 25 eV, while cluster disintegration prevails at higher energies. Similar effects are observed for larger clusters, however the energy threshold is not as sharply defined.

9:00am **TF-WeM3 On the Relative Motion of Thermal Gas Atoms In the Monte Carlo Simulation of Sputtering***, **T. Nakano**, S. Baba,* Seikei University, Japan

In this study, we have developed the treatment of gas motion in the Monte Carlo (MC) simulation of sputter deposition process. It has been known well that the mean free path of the sputtered particle depends on the speed of the particle, but the distribution function of colliding gas has been assumed to be the Maxwellian, which is independent of the particle speed.@footnote 1@ We show here that the distribution also depends on it. The collision frequency of the sputtered particle with those gases which belong to some volume in the velocity space is proportional to the product of the density of the gas, the cross section and the relative speed between the sputtered particle and the gas atoms. Therefore, the colliding gas velocity does not obey the stock Maxwellian but the one weighed by the relative speed. This distribution function can be integrated by using the relative speed and the gas speed (in laboratory system) as integrating parameters, hence it is applicable to the MC simulation. Using this method, time evolutions of velocity and positional distributions of sputtered particles are calculated and demonstrated. It is shown that the speed distribution of the sputtered particles after some period of time is described well by the Maxwellian of the same temperature with the gas. It is also shown that this method has enabled the accurate calculation of the resident time of sputtered particles in the chamber, which leads the spatial density of the particle. @FootnoteText@ @footnote 1@G. M. Turner, et al., J. Appl. Phys. 65 (1989) 3671.

9:20am **TF-WeM4 Self-Similar Structure Evolution and Surface Reaction Kinetics in Low Temperature Silicon Deposition***, **G.N. Parsons**, K.R. Bray, A. Gupta,* North Carolina State University

A current challenge in low temperature thin film deposition is to analyze energetics and kinetics of surface processes to control growth reactions and improve material properties. In this work, surface transport kinetics during silicon plasma deposition are determined by analyzing time and temperature dependent surface topography in comparison to dynamic scaling models. For plasma deposition of silicon using silane or silane/helium mixtures at 25 - 350Â°C, static and dynamic scaling parameters determined from atomic force microscopy are consistent with self-similar fractal geometry. Comparing parameters with those expected from linear continuum models indicates indicate that surface transport is dominated by adspecies diffusion with a diffusion activation barrier of 0.2eV, consistent with previous empirical estimates. However, the elementary steps associated with initial film growth are still not clear. The observed increase in diffusion length with increasing temperature contradicts some current published growth models, and ab-initio analysis of precursor adsorption reactions indicate that silyl radicals do not directly adsorb onto Si-H bonds to form 3-centered bonds, as is commonly proposed. When helium is replace by argon, significant departure from self-similar structure is observed, consistent with excess energy from surface bombardment of heavier Ar ions. Diluting silane with hydrogen results in significant changes in scaling coefficients, indicating that an additional non-linear term is needed in the continuum model to describe surface diffusion. All of the results suggest that atomic hydrogen generated in the plasma plays an important role in assisting surface transport. Possible elementary surface reactions consistent with observed results will be presented and discussed.

9:40am **TF-WeM5 Atomic-Scale Processes in the Growth of Transition-Metal Nitrides***, **D. Gall**, C.-S. Shin, M.A. Wall, I. Petrov, J.E. Greene,* University of Illinois, Urbana

Polycrystalline and epitaxial layers of NaCl-structure transition-metal (TM) nitrides -- TiN, ScN, CrN, and TaN -- were grown on oxidized Si and MgO(001) at 450-1000 °C by ultra-high-vacuum magnetically-unbalanced magnetron sputter deposition in pure N@sub 2@ and N@sub 2@+Ar discharges at 3-20 mTorr. Polycrystalline layers grown under low ion-irradiation conditions exhibit a columnar microstructure with strong 111 preferred orientation which evolves in a kinetically-limited competitive growth mode due to a large anisotropy in adatom mobilities and binding energies. Surface diffusion energies E@sub s@ were obtained from T-dependent nucleation length measurements using STM and by ab-inito density functional calculations. E@sub s@ for (001) and (111) TiN surfaces are 0.8 and 1.7 eV. The much smaller 111 adatom mobility results in preferential 3D growth and, ultimately, in the observed 111-preferred orientation. However, increasing the energy of incident N@sub 2@@super

+@ ions during deposition to 20 eV results in layers with purely 001-texture. The high anisotropy in adatom mobilities gives rise to another unique microstructural feature: epitaxial 001-oriented layers exhibit self-organized arrays of 1-nm-wide nanopipes which are formed as a result of periodic kinetic surface roughening and subsequent atomic self-shadowing. While the microstructures of different NaCl-structure TM-nitrides are similar, their electronic and optical properties vary widely. TiN has metallic conductivity, ScN is semiconducting, and CrN is an antiferromagnetic insulator. The color of Ti@sub 1-x@Sc@sub x@N varies continuously with x from golden yellow to orange to burgundy to blue-green to transparent. Measured hardness of single crystal 001-oriented layers are 20, 21, 28, and 31 GPa for TiN, ScN, CrN, and TaN, respectively.

10:00am **TF-WeM6 Low Temperature Synthesis of Fully Textured Highly Oriented AlN Films by RF and Pulsed DC Reactive Sputtering***, **G.F. Iriarte**, F. Engelmark, I.V. Katardjiev,* Uppsala University, Sweden*; H.P. Loebl,* Philips GmbH, Germany

Textured as well as epitaxial thin AlN films are of great interest for a wide range of electro-acoustic and optoelectronic applications. Reduction of the deposition temperature is of vital importance in a number of applications due to thermal budget limitations. In this work we study systematically the influence of the process parameters on the film properties and identify the mechanisms leading to improved film quality as well as reduced deposition temperature with both RF and pulsed DC sputtering in an Ar/N@sub 2@ atmosphere. It is demonstrated that fully textured (0002) films are grown under a wide range of conditions. At the same time the FWHM of the rocking curve of the (0002) XRD peak is found to vary systematically with process conditions - depostion rate, process pressure and gas composition, substrate temperature and bias. The best films show a FWHM of 1.2@super o@. By comparing RF and pulsed DC sputtering we have identified the major mechanisms leading to the synthesis of high quality films. Thus it has been found that by far the most important factor is the arrival energy of the sputtered Al atoms which is primarily controlled by the process pressure. We report for the first time that fully textured AlN films with a FWHM of under 2@super o@ can be grown at room temperature. Other important factors are the ion and electron bombardment of the films, substrate temperature as well as gas composition, although their influence is not as dramatic. Generally, the film quality increases with temperature. Bias and electron bombardment within a certain range also lead to better films. Low Ar/N@sub 2@ ratios also result in improved film quality although the mechanisms are not fully understood.

10:40am **TF-WeM8 A Theoretical Study of the Chemical Vapor Deposition of (100) Silicon from Silane***, **J.K. Kang**, C.B. Musgrave,* Stanford University

We use quantum chemistry to investigate the chemical vapor deposition of (100) silicon from silane. The CVD reaction proceeds through four sequential steps. The first step is activation of surface sites through H2 desorption from the Si (100)-2x1 monohydride surface. We find that H2 desorption proceeds through a two-step pathway. The barrier for the first step is 35.1 kcal/mol while the second step proceeds with a barrier of 31.1 kcal/mol. Next, dissociative adsorption of SiH4 occurs, where SiH3 and H fragments add to two surface dangling bonds. We find the barrier to adsorption to be 4.3 kcal/mol. Then, adsorbed SiH3 transforms directly to SiH2 through simultaneous H migration from adsorbed SiH3 to the dimer and through a dimer-opening and ring-closing reaction with a barrier of 70.7 kcal/mol. We also find an alternative path where adsorbed SiH3 transforms to SiH2 through two sequential steps in the presence of atomic H. One pathway proceeds through hydrogen abstraction from the adsorbed SiH3 on the surface with a barrier of 0.4 kcal/mol followed by a dimer-opening and ring-closing step with a barrier of 23.3 kcal/mol. An alternative path proceeds through abstraction of H from the dimer and has a barrier of 0.2 kcal/mol followed by dimer-opening and ring-closing steps with a barrier of 32.9 kcal/mol. Finally, a dihydride surface with SiH2(a) formed through dimer-opening and ring-closing reactions transforms to a monohydride surface with SiH(a) through two-sequential steps of H2 desorption from one side of dimer followed by H migration from the other side of the dimer. The predicted barrier for this H2 desorption is 47.1 kcal/mol while that for H migration is 2.8 kcal/mol. In addition, we find that the overall theoretical barrier of 60.6 kcal/mol for H2 desorption is in a good agreement with the experimentall barrier (58.2 +/- 2.3 kcal/mol).

11:00am **TF-WeM9 Gas and Surface Reactions of Radicals in Hot Wire CVD of Amorphous Silicon***, **H.L. Duan**, G.A. Zaharias, S.F. Bent,* Stanford University

Hot wire chemical vapor deposition (HW-CVD) is a relatively new growth method that has been shown to produce amorphous and microcrystalline silicon materials of superior quality in comparison to the more conventional plasma enhanced chemical vapor deposit ion (PECVD). By using this technique, the precursor molecule such as silane is dissociated on a metal filament (wire) heated to high temperature. Radical species produced from the filament subsequently either diffuse to the substrate to form the film or react to form secondary products. In this study, a laser-based soft ionization method utilizing the ninth harmonic of a Nd:YAG laser has been applied for the first time to probe various silicon-containing species simultaneously during the growth process. In addition to the detection of gas phase radicals, multiple internal reflection infrared spectroscopy is used to characterize the hydride bonding and film structure. Surface and gas phase species are followed as a function of important growth parameters such as filament temperature, filament material and substrate temperature. It is shown that Si, SiH@sub 3@, and Si@sub 2@H@sub 6@ are the major silicon-containing species evolved upon activating silane with the hot wire. However, even at low gas pressure the filament condition and chamber history are found to influence the radical species produced. Further study of the gas species generated by W and Re filaments at wire temperatures between 1000@super o@C and 2000@super o@ C indicates that heating the fil ament to higher temperatures increases the flux of Si, SiH@sub 3@, and Si@sub 2@H@sub 6@ differently. Above 1800@super o@C, the Si intensity saturates, while SiH@sub 3@ and Si@sub 2@H@sub 6@ show a monotonic increase without saturation up to 2000@super o@C. A growth mechanism consistent with these observations will be discussed.

11:20am **TF-WeM10 In-Situ Determination of the Deposition Chemistry During BPSG Dielectric Thin Film Growth***, **L.D. Flores**, J.E. Crowell,* University of California, San Diego

Dielectric thin film growth of boron and phosphorus doped silicate glass (BPSG) has been studied using the atmospheric pressure reaction between trimethylborate (TMB), triethylphosphite (TEPi), tetraethoxysilane (TEOS) and ozone (O@sub 3@). In-situ gas-phase transmission FTIR spectroscopy was performed between 400-600°C by probing the variable region between the injector, heated Si wafer and exhaust zones. These studies involve low temperature ozone initiated deposition of dielectric thin films using a new atmospheric-pressure chemical vapor deposition (APCVD) reactor utilizing a commercial monoblok vent assembly. We compare the products of N@sub 2@ / O@sub 2@ / O@sub 3@ reactions with BPSG film forming precursors while varying their reactant ratios and corresponding flow rates. The products produced during the reaction of TEOS and ozone are compared to those products measured during dopant reaction and incorporation from TMB and/or TMPi addition. Absorbances due to isolated silanol species (3737 cm@sup -1@) have been quantitatively followed as a function of input reagent concentration and distance from the injector inlet. The silanol groups and their reactions with boron and phosphorus dopant sources has been investigated in order to clarify their role in the oxidation process and to determine the reaction mechanism. Chemical pathways unique to elemental B-P-Si-O-C containing species will be presented with an emphasis placed on their role during the hydrolysis and polycondensation process leading to siloxane formation and BPSG network film growth.

Tribology
Room 132 - Session TR+SS-WeM
Fundamentals of Tribology & Adhesion

Moderator: S.M. Aouadi, University of Nebraska - Lincoln

8:20am **TR+SS-WeM1 Bonding and Debonding in Nanometer-Scale Viscoelastic Contacts***, **M. Giri**, D.B. Bousfield, W.N. Unertl,* University of Maine

Contact to viscoelastic materials, unlike elastic or elastomeric materials, are poorly understood, primarily because of the hysteretic effects caused by the time dependent mechanical properties. We present a quantitative analysis of contacts to viscoelastic materials, specifically crosslinked styrene-butadiene and uncrosslinked styrene-acrylate copolymers. Contacts were made with ultra-low load indentation using diamond probes of various axisymmetric shapes. Both creep and loading-unloading (bonding-debonding) measurements were made for penetration depths ranging from a few nanometers up to a few micrometers. This data was analyzed using the cohesive zone model recently developed by Hui and coworkers.@footnote 1@ This model demonstrates that the most information that can be extracted from a contact experiment is the Mode I Stress Intensity Functional K@sub I@. We show that no knowledge of the interfacial bonding mechanism is required to determine K@sub I@ from the displacement versus load data. In effect, K@sub I@ is analogous to the rate constant of a chemical reaction. Its measurement does not require knowledge of the bonding mechanism, but once measured, it can be used to test models of the mechanism. We illustrate this by testing the widely used bonding-debonding theory of Schapery@footnote 2@ for propagation of cracks at viscoelastic interfaces. We show that this model is inadequate to explain our results and attribute this failure to the assumption of a rate-independent interaction potential. @FootnoteText@ @footnote 1@Y.Y. Lin, C.K. Hui, J.M. Baney, J. Phys. D: Appl. Phys. 32 (1999) 2250. @footnote 2@R.A. Schapery, Intl. J. Fracture 39 (1989) 163.

8:40am **TR+SS-WeM2 A Multi-Scale Elasto-hydrodynamic Contact Model of Chemical Mechanical Planarization***, **A. Kim**, J. Tichy, T.S. Cale,* Rensselaer Polytechnic Institute

We present a physically based multi-scale finite element model to help better understand the CMP process. We extend a model that is presented in Ref. 1. This extended "soft" elasto-hydrodynamic contact model captures the fundamental mechanical and tribological aspects of the CMP process and requires few ad hoc assumptions or adjustable parameters. Recent experimental results show that fluid suction pressures exist,@footnote 2@ and the friction coefficient decreases as the Hersey number (i.e., viscosity*velocity/ pressure) increases.@footnote 3@ These results indicate that there exist mixed direct solid-solid contact and partial fluid lubrication, i.e., elasto-hydrodynmic lubrication. The theoretical results presented in this work support elasto-hydrodynamic contact (abrasion) at the pad-wafer interface. The constitutive equation for the soft polymer pad material must be some form of large strain nonlinear elasticity such as hyperelasticity as the strains of a well-deformed asperity are of order one. A physically based asperity-scale hyperelastic model, which includes a frictional effect, is presented to calculate local stresses at asperity tips. These local stresses are directly related to widely accepted material removal models. In most CMP tools, the external downward force is applied to the wafer-carrier head through a ball joint, which in principle cannot transmit a moment. In order to obtain closure of the analysis, the mean depth into the pad and tilt angle of the wafer are determined by the normal global force applied and momentum balances using the Levenberg-Marquardt method. Finally, we summarize our approach to linking the asperity scale contact analysis to the wafer scale model through a statistical method. @FootnoteText@@footnote 1@J. A. Tichy, J. Levert, L. Shan and S. Danyluk, J. Electrochem. Soc. 146(4), 1523 (1999). @footnote 2@L. Shan, Ph.D. Thesis, Georgia Institute of Technology, 2000. @footnote 3@Y. Moon, Ph. D. Thesis, University of California, Berkeley, CA, 1999.

9:00am **TR+SS-WeM3 Comparative Energy Dissipation in Nanoscale Shear and Tensile Interactions***, **G. Haugstad**,* University of Minnesota

A case study of ultrathin polyvinyl alcohol films is presented, comparing energy dissipation in three modes of scanning force microscopy: friction force, pulsed force mode and "tapping mode". Relative energy dissipation is measured on three distinct film components: a continuous first layer (~1 nm thick) strongly adsorbed to mica; a thicker, discontinuous overlayer, autophobically dewetted from the first layer; ordered overlayer islands (1 nm thick) located within the breaks of component #3. These films are chemically homogeneous but structurally heterogeneous. The components differ in amorphous content (free volume) and confinement, giving rise to differences in energy dissipation. Energy dissipation during sliding is quantified as friction force multiplied by a sliding distance of one contact diameter. Dissipation per cycle during vertical cantilever oscillation is quantified from the cantilever phase lag and the ratio of reduced to free resonance amplitude, via the method proposed by Cleveland et al.@footnote 1@ Dissipation during pull-off in pulsed force mode is quantified with a newly proposed method: by measuring the cantilever deflection with high time resolution (5 MHz) and comparing the (slowly damped) free oscillation amplitude (squared) immediately following pull-off to the quasistatic deflection (squared) immediately prior to pull-off. Corrections arise from (a) the relationship between linear deflection and (measured) angular tilt near the end of the cantilever;@footnote 2@ (b) the excitation of higher cantilever eigenmodes@footnote 2@ upon pull-off. Our results demonstrate that energy dissipation contrast in pulsed force and "tapping" modes is very similar, though the time scales of interaction are very different, whereas contrast in sliding friction is markedly different from either. @FootnoteText@ @footnote 1@J. P. Cleveland, B. Anczykowski, A. E. Schmid and V. B. Elings, Appl. Phys. Lett. 72, 2613-2615 (1998). @footnote 2@H. J. Butt and M. Jaschke, Nanotechnology 6, 1 (1995).

9:20am **TR+SS-WeM4 A Nanoscale JKR Test for Adhesive Contacts to Polymers***, S.A.S. Asif,* Geo-Centers*; **K.J. Wahl**,* Naval Research Laboratory

Contact mechanics measurements at the nanoscale are important for understanding the behavior of ultrathin films developed for adhesives, electronics packaging, microelectromechanical devices, colloidal particles, and lubrication. Determining surface mechanical properties of small devices, thin films or small volumes may be impossible by traditional methods, which lack either high spatial resolution or surface sensitivity. In this paper, we present a dynamic nanoscale Johnson-Kendall-Roberts (JKR) test to examine adhesive contacts to polymers and thin films. The nanoscale JKR test, based on a depth-sensing nanoindenter with AC force modulation capabilities,@footnote 1@ combines measurements of load and contact or interaction stiffness as a function of tip-surface separation and indenter penetration depth. With this method, and appropriate contact mechanics, it is possible to make localized mechanical property measurements (e.g. loss and storage moduli, adhesion energy, cohesive stress, and strain energy release rate) for contacts with diameters smaller than the optical limit. We present results of studies using probes with tip radii between 1 and 10 microns against polydimethyl siloxane surfaces with varying cross-link densities. Smaller probe diameters and increased cross-link density shifted the measured response away from a pure JKR model into the Maugis-Dugdale transition regime. The storage modulus and surface energy measured from nanoscale JKR results are compared to both calculated values and those measured with conventional nanoindentation. @FootnoteText@ @footnote 1@ S.A. Syed Asif, K.J. Wahl, and R.J. Colton, Rev. Sci. Instrum. 70 2408-2413 (1999).

9:40am **TR+SS-WeM5 Combined Nanoindenter and Quartz Crystal Microbalance Studies of Realistic Tribological Contact***, **B. Borovsky**, J. Krim,* North Carolina State University*; S.A.S. Asif, K.J. Wahl,* Naval Research Laboratory

There has recently been increased interest in studying friction at nanometer and micron length scales at much higher speeds than are obtainable with instruments such as atomic force microscope and surface forces apparatus. Sliding contacts in computer hard drives, micromachines, and many macroscopic applications move at speeds on the order of 1 m/s. This speed regime is routinely accessed by the vibrating surface of a quartz crystal microbalance (QCM). We have therefore constructed a device capable of studying both high-speed sliding friction and contact mechanics by combining a nanoindenting probe and QCM. By measuring normal load, contact stiffness, and QCM response simultaneously, this combination is well-suited to developing the theoretical understanding of probe-QCM systems. In order to establish the relationship between the QCM response and the properties of the interface, we have carried out detailed studies of glass-metal and metal-metal contacts in air. The interfaces are characterized by a contact area (derived from the square of the contact stiffness) proportional to the normal load, consistent with multi-asperity contact and elastoplastic deformation.@footnote 1@ We observe that the frequency shift of the QCM is proportional to the true area of contact as inferred from the contact stiffness. Following an earlier suggestion, we model the interaction in the near-field acoustic regime.@footnote 2@ We find that our results are explained by accounting for the roughness of the opposing surfaces. The magnitude of QCM frequency shift is found to reflect the elasticity of the interface, the number and size of contact regions, and the degree of slippage. Research supported by NSF, AFOSR, and ONR. @FootnoteText@ @footnote 1@ J.A. Greenwood, in Fundamentals of Friction: Macroscopic and Microscopic Processes, NATO ASI Series, I.L. Singer and H.M. Pollock, eds., (Kluwer, Boston, 1992) p. 37. @footnote 2@ A. Laschitsch and D. Johannsmann, J. Appl. Phys. 85, 3759 (1999).

10:00am **TR+SS-WeM6 Molecular Layer Effects on Friction Between Single Crystalline Metal Surfaces***, **A.J. Gellman**,* Carnegie Mellon University*; J.S. Ko,* Merck & Co.

The combined use of an ultrahigh vacuum tribometer and a variety of surface science techniques has enabled us to explore the tribological properties of interfaces between Ni(100) surfaces and to observe phenomena attributable to molecular layering. Friction measurements have been made between a pair of clean Ni(100) surfaces, modified by the presence of adsorbed atomic sulfur with and without adsorbed ethanol. Friction measurements made with ethanol coverages ranging from 0 â€“ 10 monolayers on each Ni(100) surface reveal that the friction coefficient is discontinuous in coverage and can be correlated to the coverage dependence of the ethanol desorption energy. During shearing sliding never commences between clean Ni(100) surfaces or sulfided Ni(100) surfaces without adsorbed ethanol. In the submonolayer coverage regime of either atomic sulfur or adsorbed ethanol the behavior is characterized by a high friction coefficient (µ@sub s@ > 5.5) accompanied by high adhesive forces (µ@sub ad@ = 1.5 Â± 0.7). An abrupt decrease in both the friction coefficient and adhesion coefficient occurs at a coverage of one monolayer of ethanol on each surface. The friction coefficient drops to (µ@sub s@ = 3.1 Â± 1. while the adhesion coefficient is lowered to µ@sub ad@ ~ 0.25. At coverages between 1.0 and 2.5 monolayers of ethanol on each Ni(100) surface the static friction coefficient decreases in a step-wise manner that is correlated with discontinuities in the ethanol desorption energy. This step-wise decrease in both the friction coefficient and the desorption energy may be due to molecular layering of the ethanol.

10:20am **TR+SS-WeM7 The Effect of Packing Density on the Friction of Alkane Monolayers***, **J.A. Harrison**, P.T. Mikulski,* United States Naval Academy **INVITED**

Hydrocarbon materials have traditionally been used to prevent the friction and wear of mechanical components in sliding contact. One important example of this is the use of oil in conventional combustion engines. The advent of chemical vapor deposition technology has piqued interest in the use of solid hydrocarbons as lubricants in systems such as microelectromechanical devices. A detailed knowledge of the molecular-scale mechanisms responsible for lubrication would be invaluable in the design of novel solid lubricants. We are using molecular dynamics to examine the atomic-scale phenomena governing the tribology of hydrocarbon-containing systems. Because liquid hydrocarbons and boundary layer lubricants, such as self-assembled monolayers, are to be studied, the potential energy function must include intermolecular interactions. The new adaptive intermolecular reactive empirical bond-order potential (AIREBO)@footnote 1@ can simulate reactive and non-reactive processes in a wide range of environments, including graphite, liquid hydrocarbons, and self-assembled monolayers. We have conducted extensive simulations that have examined the friction of alkane monolayers attached to diamond surfaces or model self-assembled monolayer systems. We have examined friction as a function of packing density, chain length,@footnote 2@ and sliding direction. Recent AFM results of Perry and coworkers@footnote 3@ unambiguously demonstrate that decreasing the packing density, or the disorder of the film, increases the friction. Simulations reproduce this trend and provide an atomic-scale explanation for this observation. *Supported by ONR and AFOSR. . @FootnoteText@ @footnote 1@ S. J. Stuart, A. B. Tutein, and J. A. Harrison, J. Chem. Phys. 112, 6472-6486 (2000). @footnote 2@ A. B. Tutein, S. J. Stuart, and J. A. Harrison, Langmuir 16, 291-296 (2000); Ibid. , J. Phys. Chem. B 103, 11357-11365 (1999). @footnote 3@ Lee et al., Langmuir 16 2220 (2000).

11:20am **TR+SS-WeM10 A Study of Triboelectricity on Dielectric Surfaces by Measuring Electric-discharge Luminescence during Friction***, **T. Miura**, I. Arakawa,* Gakushuin University, Japan

Triboluminescence during friction between a spherical surface and a flat surface of dielectrics, i.e., a typical pin-on-disk technique, was observed by a spectrometer and an optical microscopy. Spectrum measurement of the luminescence in ambient air made it clear that electric discharge occurs around a contact point. To investigate a relation between the electric discharge and triboelectricity the luminescent intensity distribution along the sliding direction was measured using the microscope with only UV-translucent filter. In short, the breakdown characteristics depending on the gap distance was aimed. When it is assumed that the UV distribution indicates electric discharge currents at each gap distance, the distribution is accounted for a well-known equation of semi-empirical discharge-current. As a result, voltage between the both sides was evaluated. Then the surface charge density at immediately after the friction in several ms was shown. We believe this is innovative technique to evaluate electric potential difference of triboelectricity between dielectric surfaces. In this conference we will present our experimental results, methods, analysis, and discussions in detail.

Vacuum Science & Technology
Room 125 - Session VST-WeM

Gas Sorption Phenomena I

Moderator: K.M. Welch, Consultant

8:40am **VST-WeM2 Hydrogen Equilibrium Relation for Stainless Steel***, **B. Zajec**, V. Nemanic,* ITPO, Institute of Surface Engineering and Optoelectronics, Slovenia

The thermodynamic equilibrium relation for hydrogen concentration in metal is usually described by the solubility, (Sieverts law), determined by fast and inaccurate methods. These data and the diffusivity were usually applied as the starting point for calculations of hydrogen outgassing kinetics (q@sub out@) during thermal treatment of stainless steel, proceeded to achieve as low as possible q@sub out@ at room temperature. This, in turn, sets the requirement for a large pumping speed when the ultimate pressure in the chamber should be in the extreme high vacuum (EXV) range. In general, such calculations do not match well with the observed data. In the present study, hydrogen sorption and desorption kinetics close to equilibrium was investigated by the sensitive gas accumulation method. The pressure was monitored by means of a spinning rotor gauge just before the pinch-off and for the following next months at two stabilised temperatures: 25 ° C and 55 ° C. Prior to the measurement, the stainless steel test cell of uniform wall thickness 0.15 mm, volume 125 cm @super 3@ and inner surface 460 cm@super 2@ was pumped during bake-out at 200 ° C for several days. The quantity of released hydrogen during the whole procedure equalled the concentration change @DELTA@ C=8.8 x10@super 16@ atoms H/cm @super 3@. After the pinch-off at room temperature at 4x10@super -4@ mbar, the hydrogen pressure slowly declined with an initial rate dp/dt (328K) = 6.2x10@super -11@ mbar s@super -1@ and then afterwards straightened to a state, which could be termed as an equilibrium. In similar reported experiments, where measurements started in ultra high vacuum (UHV), the dp/dt was always positive and almost constant over several orders of magnitude. A sudden change of temperature of 30 K was applied a few times to investigate the stability of the equilibrium and the change in the reaction rate. The results are compared with: new experimental data on hydrogen content in stainless steel and the equilibrium relation, particularly with present models of hydrogen outgassing in relation to UHV and EXV.

9:00am **VST-WeM3 New Results on Outgassing of Stainless Steel and Insulators***, **L. Westerberg**,* Uppsala University, Sweden*; N. Hilleret, B. Versolatto,* CERN, Switzerland*; B. Hjörvarsson,* Royal Inst. of Technology, Sweden **INVITED**

A series of outgassing measurements of 316LN stainless steel have been performed at CERN, using a standard Fischer-Mommsen test dome. Very large, 1.5 mm thick, sheets were rolled in spiral form, open in both ends, and was mounted into the test chamber. Total areas of up to 13 m@super 2@ were used in order to increase the accuracy of the measurements. Four series of bakeouts have been performed: 1. Six 48 h bakeout cycles under vacuum to 300°C; 2. One bakeout under vacuum to 450°C; 3. Five bakeouts in air to 450°C followed by one bakeout to 300°C; 4. A sample vacuum fired at 1100°C was exposed to six bakeouts at 300°C. The outgassing rates are lowered from cylce to cycle and are in the 10@super -13@ to 10@super -16@ mbar l s@super -1@ cm@super -2@ ranges, depending on the sample. For comparison and for further understanding of the underlying processes in outgassing of stainless steel we have performed a different type of experiment at the Tandem Accelerator in Uppsala, namely hydrogen depth profile measurements like in ref.,@footnote 1@ where extraction measurements of H from stainless steel at 1000 °C were compared to the average hydrogen concentrations from 50 to 700 nm measured by the @super 1@H(@super 15@N,@alpha@ + 4.3 MeV @gamma@)@super 12@C nuclear resonance reaction at 6.4 MeV. For the present experiment we have performed similar H concentration measurements on small samples which were cut out from each of the four large test sheets after the outgassing measurements were completed. @FootnoteText@ @footnote 1@L. Westerberg et al., Vacuum 48(1997)771.

9:40am **VST-WeM5 Simulation of Hydrogen Outgassing in a Fusion Device and a UHV Chamber by Recombination Limited Model***, **K. Akaishi**,* National Institute for Fusion Science, Japan*; M. Nakasuga,* Kyoto University, Japan*; Y. Funato,* Suzuka National College of Technology, Japan

Recently it has been asserted by Moore and Nemanic that hydrogen outgassing from stainless steel should be considered by recombination limited model, and they have proposed to use a thin-walled chamber of stainless steel. So we attempted to calculate the recombination rate of hydrogen at a metal surface by solving numerically one dimensional diffusion equation. The calculation were made for two cases: the redesorption rate of hydrogen implanted into the wall of a fusion device during hydrogen pulse discharge, and the hydrogen outgassing rate of a vacuum chamber during baking and in post-baking. For the second case, it was assumed that the initial hydrogen distribution in the wall before baking is uniform, hydrogen desorption occurs only on the vacuum side, and hydrogen permeation from the air side is negligible. As a result of numerical calculation, we will discuss the effect of thin wall on achieving a low outgassing rate in a short time by baking, the role of surface layer such as oxide layer, and so on.

10:00am **VST-WeM6 Hydrogen Diffusion under Reactor Irradiation***, **G.W. Schwarzinger**, M.J. Higatsberger,* Vienna University, Austria*; R.W. Dobrozemsky,* Vienna University of Technology, Austria

Diffusion of Hydrogen is of crucial and still growing importance in a variety of technical applications. In this work, the special case of hydrogen diffusion under fission reactor irradiation in stainless steel tubes of AISI types 304N and 316L is presented. Whilst the basic data had been presented in earlier publications,@footnote 1,2@ the contents of this work provide new insights resulting from a detailed sophisticated analysis of the complete data set. This revealed a previously hidden influence of the reactor irradiation on the pressure dependence of hydrogen diffusion through the samples. The pressure dependence of hydrogen permeation decreased under reactor irradiation with a half-life of approx. 150 hours. With the reactor shut off, this effect was reversed with approx. the same time constant. Based on the conditions of the experiments, a selection of interpretations for possible underlying mechanisms for the given effects are discussed. @FootnoteText@ @footnote 1@ R. Dobrozemsky, G.W.Schwarzinger and C. Stratowa, Proc. of IVC8, 15 (1980) @footnote 2@ G.W. Schwarzinger and R. Dobrozemsky, J Nucl Mater 122 & 123, 1560 (1984) .

10:20am **VST-WeM7 Thermal Desorption Study of Austenitic Stainless Steels***, J.-P. Bacher, C. Benvenuti, **P. Chiggiato**, M.-P. Reinert, S. Sgobba,* CERN, Switzerland*; A.-M. Brass,* Université Paris-Sud, France

Residual hydrogen in stainless steel results in a steady outgassing from vacuum chamber walls, hindering the achievement of UHV conditions. The total content, the binding states and the diffusivity of residual hydrogen in austenitic stainless steels, which together define the room temperature hydrogen outgassing rate, have been investigated by Thermal Desorption Spectroscopy (TDS). Eight different steel types have been studied by means of two different TDS systems. The study has been extended to the effects of various post-production treatments, aimed at reducing the hydrogen content and/or outgassing, namely vacuum firing and bakeout both in air and under vacuum. A large variety of hydrogen desorption peaks has been observed, which have been attributed to diffusible hydrogen, hydrogen trapping in the surface oxides or in lattice defects induced by precipitates, and steel recrystallisation. The hydrogen depletion effectiveness of vacuum baking at different temperatures has been quantified, and the consequences of air baking have been clarified, leading to practical guide-lines for technological applications.

10:40am **VST-WeM8 Outgassing Measurements of Stacked Laminations for Use as an Electromagnet Core***, **Y. Saito**, Y. Sato, T. Kubo,* KEK-High Energy Accelerator Research Organization, Japan

Electromagnets, involving ferrite or lamination cores, are often installed in a vacuum of accelerator system so as to bend and extract the beam. Outgassing from the cores is one of the problems, since it causes a poor vacuum, thus shortening a beam lifetime and also inducing an electrical breakdown. Outgassing measurements by a throughput method were carried out for laminations with a few kinds of insulating coatings; a quasi-inorganic and inorganic materials. It is to be noticed that the outgassing rates for loosely- and closely-stacked lamination cores do not show any significant difference for each coating, when the pumping period is as long as 100 hours, or more. Further, though pre-baking of the laminations is effective to shorten the pumping period, once exposed to atmospheric air with humidity, the outgassing rate again shows a larger value. Probably, the adsorbed/absorbed water molecules on/in the coatings require an activation energy to desorb, while, once desorbing, they can diffuse more easily, even in a narrow gap of several microns or less. This indicates that the pump-down characteristic is dominated by the coating materials, rather than by a gap distance between laminations. Indeed, stainless-steel laminations without any coatings showed much lower outgassing rates, even when closely stacked. Further, a time lag in the pump-down characteristic of the closely stacked laminations (a 100 mm-square sheet) is estimated to be several hours by a Monte-Carlo simulation, being shorter than 100 hours of pumping.

Applied Surface Analysis
Room 134 - Session AS-WeA
Depth Profiling II

Moderators: L. Kövér, Institute of Nuclear Research of the HAS, Hungary, A.T.S. Wee, National University of Singapore

2:00pm **AS-WeA1 Multi-Technique Analysis of the Paint/Sealant Interface in Aircraft Structures*, S.J. Harris,*** British Aerospace, UK **INVITED**

The changes in environmental legislation in the early1990's following the Montreal Agreement has resulted in the need for changes in the surface treatments used in the aerospace industry. This involves the removal of the CrVI ion from all processes and the use of low VOC (volatile organic content) or water based coatings. MaSSPS (or Materials System for Surface Protection and Sealing, a Brite-Euram project, BRPR CT-97-0538), incorporating 11 partners, aims to develop a fully integrated corrosion protection system using both of the above ideals. The system will consist of a Cr-free conversion coating, low VOC and water based, Cr-free primers, a Cr-free low density, fuel/water resistant, high adhesion sealant. The interaction of these new materials is complex and has to be understood in-order to avoid system failures in service. A key part of the airframe where these new materials will be used is the aircraft's fuel tank. This is an integral part of the wing and, therefore, the coatings and sealants will be subjected to a wide range of temperatures, fuel and fuel/water mixtures and exposure to fungi that live at the fuel/water interface. This paper will discuss one of the many problems associated with a system of this kind. The challenge is to develop analytical methods to explore the surfaces and interfaces and understand their modes of failure. The surface analytical techniques used in the project are briefly described., which include XPS, ToF-SIMS, in-situ SEM tensile testing, AFM and µTA. The work will be described in a case by case basis rather than a discussion on individual surface analytical results.

2:40pm **AS-WeA3 Fourier Modulus Brings Charging Samples, Auger Depth Profiles, Linear Least Squares and Factor Analysis Together*, D.J. Pocker,*** *M.A. Parker,* IBM Storage Technology Division*; R.E. Davis,* IBM Microelectronics Division

The shifting of Auger spectra has frustrated the extraction of chemically distinct depth profiles from charging samples using Linear Least Squares (LLS) or Factor Analysis (FA) methods. It is shown here that normal LLS or FA of the moduli (or magnitudes) of Fourier transforms of profile spectra readily yields such chemically distinct depth profiles. This approach applies equally to ESCA measurements and to line scans, maps and time sequence spectra. There are two requirements: The spectral energy window must be wide enough to capture the whole peak over its whole range of shifts. And, any given shifted spectrum cannot have stationary spectra or differently shifted spectra of other constituents superimposed on it.

3:00pm **AS-WeA4 Determination of the Depth Scale in Sputter Depth Profiling*, S. Hofmann,*** Max-Planck-Institute for Metals Research, Germany

Determination of the sputtered depth in depth profiling with high accuracy is a difficult task in quantitative depth profiling. Usually, a linear interpolation is performed between two pionts, one corresponding to the unsputtered surface (zero sputtering time), and the other to the crater depth after sputtering (maximum sputtering time) or to a previously determined marker depth (interface, delta layer etc.).@footnote 1@ This simple two point method contains a principal uncertainty because of the generation of a native oxide layer when the sample is brought back to air. In addition, this method does not take into account a composition dependency of the sputtering rate, which is particularly important in interface profiling.@footnote 2@ Furthermore, the change of the sputtering rate caused by the initial build up of the collisional cascade, and by compound formation, e.g. in reactive ion sputtering, is neglected. Using multilayer interfaces as markers, depth profiling of multilayers can markedly reduce the initial transient effect. Comparison of profiling results on Ni/Cr, Ta/Si, SiO2/Ta2O5, and GaAs/AlAs multilayers show how preferential sputtering and compound formation influence the sputtering time/depth relation. In sputter depth profiling with AES, simultaneous recording of two signals of the same element with low and high electron energies, combined with quantitative evaluation of the intensity scale, can be used to inrinsically determine the depth scale. @FootnoteText@ @footnote 1@ ISO Technical Report 15969 to be published 2001 @footnote 2@ S. Hofmann, Sputter Depth Profile Analysis of Interfaces, Rep. Prog. Phys. 61 (1998) 827.

3:40pm **AS-WeA6 ARXPS Analysis of Nitrogen Distribution and Chemistry in Nitrided Gate Oxides*, A.C. Ferryman,*** *J.E. Fulghum,* Kent State University

Rapid and reliable characterization of thin, nitrided gate oxide films remains a priority for the semiconductor industry. In this study we evaluate a variety of methods for the analysis of angle-resolved XPS data from nitrided gate oxides. The films have previously been characterized using SIMS depth profiling, and vary in oxide thickness and nitrogen location. Methods based on both ARXPS analysis of core-level photoelectron spectra and on inelastic background analysis will be compared. Trade-offs between rapid data acquisition and high energy resolution N chemistry analysis will be evaluated with respect to ARXPS results. The effect of variation in the electron attenuation length value at shallow angles will be discussed for oxide thickness measurements.

4:00pm **AS-WeA7 Characterizing Nanometer Oxy-nitride Films with ESCA Low Energy Sputter Depth Profiles,** *J.H. Gibson,* Physical Electronics*; **E.L. Principe,*** Applied Materials*; J.F. Moulder, D.G. Watson,* Physical Electronics*; A. Hegedus,* Applied Materials

Nanometer thick oxy-nitride films were used to evaluate low energy ESCA sputter depth profiling as a method to determine composition and elemental distribution within ultra thin films. Many previously published studies have focused on the use of angle resolved ESCA measurements to determine the composition of these films. The uncertainties of generating depth distribution information from angle resolved ESCA measurements are the topic of much debate and research. ESCA low energy sputter depth profiling provides a direct measurement of elemental distributions within ultra thin films and may be a valuable tool for thin film development and interpreting angle resolved ESCA measurements. Low energy sputter depth profiles and angle resolved ESCA measurements from 2 nm thick SiON films will be presented. The use and limitations of these complementary approaches for characterizing ultra thin films will be discussed.

4:40pm **AS-WeA9 Reconstruction of Buried Polymer Interfaces Observed by Sum-Frequency Generation*, L.J. Richter*,** *P.T. Wilson, K.A. Briggman, J.C. Stephenson, W.E. Wallace,* National Institute of Standards and Technology

The structure of polymer interfaces determines many in service properties such as adhesion. Linear vibrational spectroscopies (FTIR, ATIR, and Raman) are some of the most widely accepted and utilized diagnostics of bulk polymer systems but typically do not have sufficient specificity to probe interfaces. Vibrationally resolved sum-frequency generation (VR-SFG), a non-linear optical technique, is uniquely interface specific as it is dipole forbidden in media with inversion symmetry. We have developed a novel microcavity technique that allows selective characterization of the buried interfaces of polymer/polymer and polymer/dielectric thin film systems. We have applied the technique to the study of the buried interface between polystyrene (PS) and a hydrogen silsesquioxane (HSQ) spin-on-glass (Dow Corning FOx). The as-spun HSQ film is hydrophobic, with a water contact angle >90°. UV-ozone treatment of the as-spun HSQ results in a hydrophilic surface, with a water contact angle

Biomaterials
Room 102 - Session BI+AS-WeA
Surface Characterization

Moderator: D.G. Castner, University of Washington

2:00pm **BI+AS-WeA1 Sum Frequency Generation (SFG) - Vibrational Spectroscopy and Atomic Force Microscopy (AFM) Studies of Biomaterial Liquid and Gas Interfaces. Surface Structures, Compositions and Bonding*, G.A. Somorjai,*** University of California, Berkeley **INVITED**

The surface monolayers of polyethylene and polypropylene and its blends, polyurethanes with different hydrophilic and hydrophobic endgroups and their blends and pHEMA have been studied by a combination of SFG and AFM. SFG reveals the different surface structures of polyolefins as a function of molecular weight. Changes of chain orientation occur at the glass transition temperature of polypropylene (-10 ËšC). When polyethylene is stretched, the surface becomes rough as the spherulites align in the stretch direction thereby weakening the polymer normal to the stretching direction. pHEMA with polymer groups that are crosslinked and polymer chains that are not exhibit variations of friction coefficients as measured by AFM. The low friction areas can be associated with polymer chains that are not crosslinked that can also be removed by methanol solution. These studies can also be carried out while the surface is under water. AFM reveals phase separation in blends due to the difference in friction coefficients of the two polymer components.

2:40pm **BI+AS-WeA3 Quantitative Analysis of Multicomponent Adsorbed Protein Films by Static Time of Flight Secondary Ion Mass Spectrometry*, M.S. Wagner*, *M. Shen, T.A. Horbett, D.G. Castner,* University of Washington

Quantitative analysis of multicomponent adsorbed protein films is an integral part in the investigation of biofouling in many marine, food processing, and biomaterial applications. We have previously shown that Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and multivariate analysis (MVA) are ideal techniques for the analysis of single component adsorbed protein films.@footnote 1@ MVA is also essential for quantitative compositional analysis of multicomponent adsorbed protein films in one parallel ToF-SIMS experiment. Partial Least Squares Regression (PLSR), a multivariate calibration technique, can quantitatively determine the composition of binary protein mixtures adsorbed onto mica using only the single component spectra for calibration. Current research focuses on binary protein mixtures on fluorocarbon and nitrogen-containing plasma polymer surfaces, both providing unique challenges for quantitative analysis by ToF-SIMS. Ternary and quaternary adsorbed protein films adsorbed onto mica were also investigated to determine the limit of complexity for quantitative compositional analysis. Finally, Principal Component Analysis (PCA) and a set of standard spectra were used to obtain semi-quantitative compositional analysis of a time series protein adsorption from dilute plasma solutions. Factor-deficient (fibrinogen and kininogen) plasmas were studied to corroborate this data. Multivariate analysis and ToF-SIMS are useful tools for quantitative compositional analysis of multicomponent adsorbed protein films. @FootnoteText@ @footnote 1@ M. S. Wagner and D. G. Castner, Langmuir in press (2001).

3:00pm **BI+AS-WeA4 Limits of Detection and Identification for Adsorbed Protein Films using XPS, ToF SIMS and Multivariate Analysis*, S.L. McArthur*, *M.S. Wagner, M. Shen, T.A. Horbett, D.G. Castner,* University of Washington

In the ongoing development of biomaterial surfaces capable of resisting protein adsorption, surface analytical means of accurately detecting and subsequently identifying sub monolayer amounts of protein are becoming critical. The surface and chemical sensitivity of ultrahigh vacuum techniques such as XPS and ToF-SIMS have been utilized for some time in the detection of adsorbed protein films. More recently, multivariate analysis techniques have enabled the identification of the adsorbed species from both single and binary solutions via ToF-SIMS. In the instances where protein adsorption is low factors such as surface chemistry, surface coverage and roughness can be expected to complicate data interpretation, strongly influencing the both the detection sensitivity and accuracy of the protein identification. In this study a number of different surfaces were incubated in protein solutions of varying concentrations from 0.1ng/ml to 100µg/ml. Protein adsorption was quantified using radiolabelling and each surface analyzed using both XPS and ToF-SIMS. The results of the study illustrated the significant role of surface chemistry on the detection limits for adsorbed proteins. Not surprisingly, the presence of nitrogen in the substrate hindered the detection of protein by XPS, although detection limits remained high (<10ng/cm@super2@) for ToF-SIMS. The most interesting finding was the poor detection limits on PTFE surfaces, where both XPS and ToF-SIMS were unable to detect proteins below 100ng/cm@super2@. The detection limit of ToF-SIMS for protein adsorbed onto mica was 0.1 attomole of protein, rivaling the sensitivity of liquid and gas phase MS. Multivariate classification methods were also implemented to identify the adsorbed protein at submonolayer surface coverages. These results were also highly dependent on the substrate chemistry and morphology. Both XPS and ToF-SIMS are useful tools for the characterization of low levels of adsorbed protein.

3:40pm **BI+AS-WeA6 High z-resolution Microscopy of Biological Interfaces*, C.M. Ajo-Franklin*, *L.C. Kam, S.G. Boxer,* Stanford University

Total internal reflection fluorescence microscopy (TIRFM) is widely used to study the structure and dynamics of biological interfaces by confining the excitation of a complex fluorescent sample very close to the material on which it is supported. By working with high refractive index solid supports, it is possible to even further confine the evanescent field, and by varying the angle of incidence, to profile fluorescent objects with high z-resolution. High refractive index materials, such as lithium niobate, sapphire, and zinc sulfide, exhibit different surface chemistries and each presents a unique challenge for defining biomolecular assemblies at the surface, a prerequisite for high resolution TIR techniques. In contrast, many well-developed strategies exist for modifying and tethering biomolecules to SiO@sub 2@ surfaces. Furthermore, SiO@sub 2@ surfaces are one of the few that can be used as substrates for supported lipid bilayers, a useful model system for studying biological membranes and interactions between membrane components and cells. We report the fabrication of hybrid surfaces consisting of nm layers of SiO@sub 2@ on lithium niobate (LiNbO@sub 3@, n = 2.3). Supported lipid bilayer membranes can be assembled and patterned on these hybrid surfaces as on conventional glass. By varying the angle of incidence of the excitation light, we show resolution of structures near a dielectric interface displaced by only tens of nanometers. These results demonstrate that it should be possible to profile the vertical location of fluorophores with nm resolution in real time, opening the possibility of many experiments at the interface between supported membranes and living cells.

4:00pm **BI+AS-WeA7 Chiral Recognition Observed at the Molecular Level by UHV-STM: Cysteine on Au(110)-(1x2)***, A. Kühnle, **T.R. Linderoth**, B. Hammer, F. Besenbacher,* University of Aarhus, Denmark

Chirality is a frequently encountered property of organic molecules, leading to the existence of two mirror-image enantiomers. Interestingly, Nature is often homo-chiral in the sense that only one enantiomer participates in biological processes. Molecular recognition with chiral specificity is thus crucial within many fields of chemistry, biology and medicine. It is also essential for strategies to resolve racemic mixtures into enantiopure phases. Here we report on the adsorption of the chiral amino acid cysteine [HS-CH@sub 2@-CH(NH@sub 2@)-COOH] on the Au(110)-(1x2) surface under Ultra-High Vacuum conditions. Using Scanning Tunneling Microscopy (STM) we have discovered that the cysteine molecules can form isolated molecular pairs that break the mirror symmetry of the gold surface. This provides a model system for a molecular level study of chiral recognition: Deposition of the pure L and D- enantiomers, respectively, leads to identical, but mirror-reflected, cysteine pairs clearly distinguishable by STM. Most interestingly, deposition of the racemic D-L mixture only leads to the known homochiral pairs, showing that heterochiral D-L molecular interaction is avoided. To explore the origins of this novel chiral recognition mechanism, we have performed ab-initio DFT calculations. We find that the cysteine molecules are anchored to the surface via S-Au bonds and interact mutually through hydrogen bonds between the carboxylic groups. Importantly, a favorable interaction between the surface and the amino group is only geometrically feasible for homochiral pairs. The mechanism behind the observed chiral recognition is thus reminiscent of the generic so-called three-point contact model for chiral ligand-receptor interaction.

4:20pm **BI+AS-WeA8 Interactions between Calix-6-arene Sulfonates and Poly (Allylamine Hydrochloride) : A Stoichiometric Complexation Able to Release Proteins Bound to the Polyelectrolyte*, V. Ball*, *G. Esposito, A.W. Coleman, P. Schaaf,* CNRS, France*; J.C. Voegel,* Unite INSERM 424, France

In the framework of our research, aimed to understand the fundamental mechanisms of interactions between polyelectrolytes and proteins or between polyelectrolytes and ions either in the adsorbed state on surfaces or in solution, we describe here the interaction between calix-6-arene sulfonate (C6S) and poly (allylamin hydrochloride), PAH. At pH = 7.4, the C6S molecules carry 6 negative charges owing to their sulfonate groups whereas the polyelectrolyte is positively charged. Electrophoretic mobility experiments show that neutral particles are formed when the amount of negative charges coming from C6S matches the amount of positive charge from PAH (two chain lengths have been investigated). These particles display sizes in the µm range and are subjected to sedimentation after long term equilibration. Hence, coacervation occurs and this process is irreversible, since addition of either an excess of PAH or C6S does not change the solution turbidity and the particle size distribution. At smaller C6S/PAH stoichiometries, where C6S is totally removed from the unbound state in solution, the particles are positively charged and smaller in size (hydrodynamic radius between 50 and 150 nm). Therefore, the neutral particles obtained at the charge equivalence may result from aggregation of smaller C6S-PAH aggregates. Moreover, H-NMR experiments show that the C6S molecules are tightly bound to the polymer. We show then that one can make use this strong interaction in competition experiments to release quantitatively bovine serum albumin (BSA) that has been bound to PAH molecules in a previous step. These BSA-PAH aggregates are spontaneously dissociated and replaced by C6S-PAH particles which sediment, the supernatant only containing proteins in their native secondary conformation.

5:00pm **BI+AS-WeA10 Carbon Based Coatings for Cardiovascular Stents*, E.A. Evans*, University of Akron*; U. Hafeli,* Cleveland Clinic Foundation

Carbon based films including diamond like carbon have been deposited as a protective layer for coronary stenting applications. Taking advantage of carbon's stability, or resistance to chemical attack, its flexibility, and other properties, our current technical objective is to develop carbon based materials as coatings for radioactive rhenium stents. Radioactive rhenium stents are being investigated to limit smooth muscle cell growth following coronary surgery. The carbon based coating is being investigated to reduce the release of radioactive rhenium (free activity) into the blood following the stenting procedure. Plasma enhanced deposition was used to deposit the carbon based coating onto metallic substrates. Foils, wires, and coils were coated and tested for adhesion, cytotoxicity, and release of radioactive rhenium. A critical requirement for successful stenting devices is a uniform surface over the entire structure. Our initial results indicate a 50% decrease in the release of free activity relative to uncoated rhenium. Relationships between deposition parameters and coating performance will be presented.

Biomaterials

Room 103 - Session BI+NS-WeA

Nanobiology

2:00pm **BI+NS-WeA1 Light-controlled Molecular Shuttles Based on Motor Proteins***, **H. Hess**, J. Clemmens, D. Qin, J. Dennis, J. Howard, V. Vogel,* University of Washington

Molecular shuttles, an active transport system to position nanoscale objects, are needed as parts of molecular assembly stations, self-healing materials, or nanoscale actuators. The key problems of such a transport system are finding the motors, guiding the motion, loading cargo, and controlling the speed on the nanoscale. Active transport by single molecules is ubiquitous in biology and the solutions found by nature can serve as inspiration for technology. We demonstrate that molecular shuttles resembling conveyor belts can be constructed utilizing kinesin motor proteins as engines, microtubules as belts, and ATP as fuel. Two different strategies for guiding the microtubules have been explored by us: Arranging the motor proteins in nanometer-wide tracks by selective adsorption or creating micrometer-wide guiding channels by soft-lithography. Selective loading of cargo is accomplished by tagging cargo with streptavidin, and linking it to biotinylated microtubules. User-controlled exposure of caged ATP to UV-light and addition of an ATP-consuming enzyme to the buffer solution can move the microtubules in discrete steps. This forms a tool-set for the assembly of a functional molecular shuttle.

2:20pm **BI+NS-WeA2 The Direct Measurement of Drug-enzyme Interactions by Atomic Force Microscopy***, S.M. Rigby-Singleton, **S.J.B.T. Tendler**, S. Allen,* University of Nottingham, UK*; M.C. Davies,* University of Nottingham, UK, United Kingdom*; C.J. Roberts, P.M. Williams,* University of Nottingham, UK

AFM has been employed to directly probe the rupture forces upon the mechanical dissociation of the drug-enzyme complex formed between the anticancer compound methotrexate and the protein dihydrofolate reductase (DHFR). AFM probes were functionalized with methotrexate immobilized beads and rupture forces recorded between the probe and a DHFR monolayer attached via Lys residues. Three variables were studied, AFM retraction rates, the presence of the enzyme cofactor NADPH and the protonation of the key enzyme Asp26 residue. Rupture forces of 91 pN were recorded at a retract velocity of 1 micrometer per second, a ten fold decrease in velocity resulted in an observed decrease in rupture force. The influence of the enzyme cofactor was negligible suggesting little effect on the dissociation pathway, this is in marked contrast to literature fluorescent binding assays. Notably a decrease in rupture force of approximately 25pN was observed when the pH was decreased below the pKa of the key Asp26 residue which is situated deep within the methotrexate binding site. These studies indicate that the AFM will be a valuable tool in the drug discovery process.

2:40pm **BI+NS-WeA3 Single and Multiple Molecule Binding Forces Measured Using Modified Atomic Force Microscope Cantilevers***, **R.G. Rudnitsky**, F. Drees, K.S.H. Wu, T.D. Perez, W.J. Nelson, T.W. Kenny,* Stanford University

Although the energies and forces controlling protein interactions are frequently inferred from traditional equilibrium and kinetic measurements, recent developments in chemical force microscopy allow for the direct quantification of the ranges and magnitudes of binding forces between individual protein pairs and between groups of proteins. We report here on the use of specially modified Atomic Force Microscope cantilevers to measure bond strength down the single-molecule level, with pico-Newton force resolution, using the cellular binding protein E-cadherin as our model system. Previous E-cadherin studies focused on the energetics of large systems of molecules, typically in-vivo, to demonstrate their role in cellular adhesion. Our novel AFM force spectroscopy method tracks the unbinding process of single and multiple E-cadherin molecules under force loads, to quantitatively differentiate specific from non-specific binding, and single and multiple binding events, in surface bound protein. The measurements isolate the extracellular domain of the molecule, thought to be essential for stable cell adhesion, and demonstrate the dependence of binding forces at a molecular level on Ca++ concentrations. The data correlates the relationship of homophilic E-cadherin adhesion to surface protein density in a way not previously demonstrated in cellular studies.

3:00pm **BI+NS-WeA4 Selective Molecular Assembly Patterning - A New Approach to Micro- and Nanochemical Patterning of Surfaces for Biological Applications***, **R. Michel**,* Laboratory for Surface Science and Technology, Switzerland*; J.W. Lussi,* Laboratory for Biomedical Engineering, Swiss Federal Institute of Technology, Zurich, Switzerland*; I. Reviakine, M. Textor, N.D. Spencer,* Laboratory for Surface Science and Technology, Switzerland

A novel method for producing chemically patterned surfaces based on selective self-assembly of alkane phosphates on metal oxide surfaces is presented. Standard photolithography is used to create patterns of titanium oxide within a matrix of silicon oxide by successively depositing 40 nm of TiO@sub 2@, 10 nm of SiO@sub 2@ onto a silicon wafer, followed by photoresist application and anisotropic etching. Ordered SAMs of alkane phosphates form on the TiO@sub 2@, but not on the SiO@sub 2@ surfaces by self-assembly. Poly-L-lysine-g-poly(ethylene glycol) (PLL-g-PEG) is used to render the exposed SiO@sub 2@ protein-resistant. X-ray photoelectron spectroscopy and imaging time-of-flight secondary ion mass spectrometry were used to characterize the surfaces. Protein adsorption studies conclusively established that the resulting surfaces presented protein adhesive (the TiO@sub 2@/alkane phosphate SAM region) and non-adhesive (the PLL-g-PEG-coated SiO@sub 2@) areas. This novel Selective Molecular Assembly Patterning (SMAP) technique was used to grow fibroblasts in the presence of serum on 5*5 µm TiO@sub 2@ spots. Cytoskeletal organization in the fibroblasts was induced above the 5*5 µm TiO@sub 2@ patches, while no interaction with the PLL-g-PEG background was evident. The SMAP technique is considered to be highly suitable for reproducible and cost-effective fabrication of biologically-relevant patterns over large areas, by combining state-of-the-art photolithography and simple self-assembly dip-and-wash processes. Its applicability to sub-micrometer patterns is currently being evaluated.

3:20pm **BI+NS-WeA5 Studies of 20 nm Gold Particle Systems for Biosensing Applications & Optical Properties of Gold Nanostructures***, L. Olofsson, **F. Höök**, P. Delsing, D.S. Sutherland, J. Gold, B. Kasemo,* Chalmers University of Technology, Sweden

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3:40pm **BI+NS-WeA6 Nanofabricated Lipid Bilayers Patterned on Metal Electrodes***, **R.N. Orth**, I. Hafez, J. Kameoka, M. Lindau, H.G. Craighead,* Cornell University

Lipid molecules were immobilized on the surface of photolithographically patterned chromium and titanium. Large unilamellar lipid vesicles were found to bind on the native oxide surface of patterned support metals. Metal evaporation and resist liftoff techniques were used to pattern metal on a hydrophobic polymer surface. Lipids bound on solid substrates provide a biological interface for impedance measuring electrodes to detect bound cells or biomaterial. This patterning technique provides means to specifically bind lipids and conjugated biomaterials (polyethelene glycol (PEG), biotin, fluorescence dyes, and DNA oligimers) to the electrode surface. This technique may be applied to patterning biomaterial on metal inside thermally bonded microfluidic channels, to form titanium coated biomedical implants, and to create robust lipid-conjugated electrodes for biosensor applications.

4:00pm **BI+NS-WeA7 The Micropatterning of Mixed SAM Surfaces Using Inkjet Printing Technology: A Comparison Study to Microcontact Printing***, **L.F. Pardo**, T. Boland,* Clemson University

Micropatterning is a powerful method for controlling surface properties, with a myriad of applications ranging from cell biology to electronics. Self-assembled monolayers (SAMs) of alkanethiolates on gold, the structures most widely used for preparing organic films with specific surface properties, are usually patterned by partitioning the surface into regions formed from different thiols. In microcontact printing for example, patterned self-assembled monolayers (SAMs) are printed onto a surface using a polydimethilsiloxane (PDMS), made using a microfabricated mold. Although this technique is suitable, the distortion of patterns, pattern limitation to binary mixtures and expensive mold design are limiting the efficient use of stamps. In this study, a new method utilizing inkjet printing technology for patterning mixed thiols is introduced. Methyl and carboxyl-terminated hexadecanethiols were patterned onto clean gold surfaces using a modified inkjet printer. The topography of the micropatterned samples was visualized and measured by atomic force microscopy. The chemico-physical properties investigated by Fourier Transform infrared spectroscopy and dynamic contact angle measurements suggest that inkjet printer yielded high throughput patterning on surfaces. This new inkjet printing technique provides a quick and inexpensive method for micropatterning alkanethiols of surfaces.

4:20pm **BI+NS-WeA8 Fabrication of High Aspect Ratio Vertically Aligned Carbon Nanofiber-based Electrochemical Probes for the Probing of Intact Whole Cells***, **T. McKnight**,* Oak Ridge National Laboratory*; M.A. Guillorn,* Oak Ridge National Laboratory & University of Tennessee*; A.V. Melechko, D.W. Austin,* University of Tennessee*; V.I. Merkulov, M. Doktycz,* Oak Ridge National Laboratory*; D.H. Lowndes, M.L. Simpson,* Oak Ridge National Laboratory & University of Tennessee

Molecular biology and genomics are providing great insight into gene sequence, regulation and function. At the same time, imaging technology is elucidating cellular structure. Unfortunately, we have limited ability to monitor processes within and around living cells in real time and with high spatial resolution. This limitation is largely technological - our current research instruments are simply not on the same size scale as the functional components of cells. Here we present the fabrication and operation of high aspect ratio vertically aligned carbon nanofiber (VACNF)-based electrochemical probes for the probing of intact whole cells. Electron beam lithography was used to define the catalytic growth sites of the VACNFs. Following catalyst deposition, VACNF were grown using a novel plasma enhanced chemical vapor deposition (PECVD) process. Photolithography was performed to realize interconnect structures. These probes were passivated with a thin layer of SiO2, which was then removed from the tips of the VACNF, rendering them electrochemically active. We have demonstrated their functionality by selectively electrodepositing Au clusters onto the tips of the probes. We believe that these probes are ideally suited for characterizing intracellular phenomena in real time with an unprecedented degree of spatial resolution.

Dielectrics
Room 130 - Session DI-WeA
Low K Dielectrics

Moderator: Z. Yu, Motorola Labs

2:00pm **DI-WeA1 Materials Issues and Recent Development of Low k Dielectrics for Advanced Interconnects***, **P.S. Ho**,* The University of Texas at Austin **INVITED**

Materials Issues and Recent Development of Low k Dielectrics for Advanced Interconnects Low k dielectrics are being developed for on-chip interconnects beyond the 0.13 micron generation. To replace silicon dioxide, there are stringent requirements on materials properties imposed on the low k dielectrics. The challenge is how to maintain the thermomechanical properties of the material while decreasing its dielectric constant, particularly for porous materials with dielectric constant less than 2. In spite of this difficulty, several materials have been developed and process integration demonstrated recently. The materials issues and characterization of low k dielectrics will be presented. Recent developments based on optimization of molecular structures will be discussed.

3:40pm **DI-WeA6 Formation of Self-Assembled Molecular Layers on the Low Dielectric Porous Methyl Silsesquioxane***, **J.C. Hu**, C.W. Wu, L.J. Chen,* National Tsing Hua University, Taiwan, R.O.C.*; C.H. Li,* National Chiao Tung University, Taiwan, R.O.C.*; T.C. Chang,* National Sun Yat-Sen University, Taiwan, R.O.C.*; C.J. Chu,* Nanmat Technology Co., Taiwan, R.O.C.

Porous methyl silsesquioxane (PMSQ) with a low dielectric constant (~1.8) is of great interest for ULSI applications. However, many hydrophilic methyl groups (-CH@sub 3@) on the PMSQ were destroyed under O@sub 2@ plasma ashing. Hydroxyl groups (-OH) were bonded with Si dangling bonds on the PMSQ films. H@sub 2@ plasma post-treatment is usually used to decrease -OH bond formation. In the present work, bottom-up growth behavior of self-assembled molecular layers (SAMs) on the PMSQ was investigated. Diclorodimethylsilane was used to form SAMs on the PMSQ at the room temperature. Structural properties of the PMSQ films were investigated using FTIR. The absorption peaks of Si-C (781 cm@super -1@), Si-C (1273 cm@super -1@), and C-H (2975 cm@super -1@) in PMSQ samples disappeared after O@sub 2@ plasma treatment for 5 min. It indicated that the majority of methyl groups in the films were removed and Si dangling bonds were exposed. The Si-O cage-like structures in the PMSQ films also decreased due to its loose structure arrangement. As a result, the low dielectric characteristic of PMSQ would be damaged. On the other hand, the absorption peaks of Si-C and C-H were present for the PMSQ films dipped in diclorodimethylsilane solution with and without ultrasonic system. The purpose of using ultrasonic system was to accelerate formation rate of SAMs on the PMSQ. The results revealed that the hydrophobic dimethylsilane groups have been formed on the surface of PMSQ. The Si-OH bonds on the PMSQ changed to Si-O-Si(CH@sub 3@)@sub 2@. The thickness of SAMs was less than 1.0 nm. The -CH@sub 3@ groups of SAMs on the Si-O network surface of the PMSQ films were apparently of ordered array structure owing to minimal steric hindrance arrangement.

4:00pm **DI-WeA7 Temperature-dependent Current Transport in Low-k Inorganic Polymer Dielectrics***, **J.W. Tringe**, R.A.B. Devine,* U.S. Air Force Research Laboratory

Low-k dielectrics are an increasingly important class of materials for high-performance integrated circuits, promising to significantly increase processing speeds by lowering resistance-capacitance delays in global interconnects. However, since these new dielectrics are anticipated to cover large areas of the chip they also represent a potential reliability risk. It is therefore important to understand how charge transport occurs in the low-k films over a range of temperatures in order to avoid breakdown or excess leakage current during circuit operation. Low-k dielectric films based on inorganic polymers such as FOx flowable oxide from Dow Corning have been examined. Spun-on films, 3000 Å thick, were patterned into metal-insulator-semiconductor capacitor structures, then probed to measure current and capacitance as a function of voltage. Temperature-dependent current-voltage measurements, over the range 26 to 150 °C, show that current conduction is predominately via either Schottky or Frenkel-Poole emission. A field-independent thermally activated barrier height of approximately 0.1-0.2 eV is deduced. The measured exponential term proportional to the square root of the electric field in the current-voltage dependence is smaller than expected for Frenkel-Poole emission, however. Additionally, the temperature and field dependences of the exponential prefactor do not enable us to clearly distinguish between Schottky or Frenkel-Poole emission over the experimental temperature range.

4:20pm **DI-WeA8 Characterization of SiC Films for Cu/low-k Integration***, **F.G. Celii**, T. Tsui, R. Willecke, J. Large,* Texas Instruments, Inc.

Silicon carbide (SiC) is being evaluated for integration into Cu/low-k backend process flows. Potential applications include use as a patterning hardmask and as an etch stop layer with Cu diffusion properties. This paper reports the physical and optical characterization of SiC films. Films were deposited on 200 mm wafers in a commercial reactor using plasma-enhanced chemical vapor deposition (PE-CVD). Film composition and bonding were elucidated using SIMS, XPS and FT-IR spectroscopies. Optical properties of the films were determined from variable-angle spectroscopic ellipsometry into the vacuum ultraviolet region (~140 nm). Under some processing conditions, we observed ellipsometry data consistent with a vertical gradient in the SiC refractive indices. The optical constants of the film, along with reflectance modeling using Prolith, suggest SiC can be used as an anti-reflection coating (ARC) layer for lithographic patterning at either 248 or 193 nm. To test the optical modeling results, we have prepared various film stacks containing SiC and organosilicate glass (OSG) on Si or Cu. The reflectivity vs. wavelength will be measured and compared with the calculated reflectivity values. Initial patterning results will also be presented.

Wednesday Afternoon, October 31, 2001

Electronics
Room 124 - Session EL-WeA

Semiconductor Growth

Moderator: E. Rotenberg, Lawrence Berkeley National Laboratory

2:00pm **EL-WeA1 Epitaxial Growth by Low-energy Plasma-enhanced CVD*, H. von Känel,*** ETH Zürich, Switzerland*; M. Kummer, A. Dommann,* Interstate University of Applied Science, Switzerland*; C. Rosenblad, J. Ramm,* Unaxis Semiconductors, Liechtenstein*; T. Hackbarth, M. Zeuner,* Daimler Chrysler Research Center, Germany **INVITED**

Epitaxial growth of Si and SiGe by a low-energy plasma-enhanced CVD (LEPECVD) process is described. LEPECVD is based on a low voltage DC arc discharge, leading to very efficient decomposition of the gaseous precursors SiH@sub 4@ and GeH@sub 4@. In addition, direct immersion of the substrate in the intense plasma strongly enhances surface kinetics in particular at low growth temperatures. As a result, epitaxial growth rates in LEPECVD can be as high as 10 nm/s, nearly independent of the substrate temperature in the range between 500°C and 750°C. LEPECVD is ideally suited for the growth of SiGe-MODFET and SiGe-MOSFET structures, requiring thick graded Si@sub 1-x@Ge@sub x@ buffer layers with low defect densities. Concentration profiles are easy to control because Ge incorporation is entirely determined by the germane to silane flux ratio. X-ray reciprocal space mapping, defect etching and scanning force microscopy have been used to characterize buffers grown with Ge end concentrations between 10 % and 100 %. LEPECVD combined with other low temperature growth techniques, such as molecular beam epitaxy (MBE) has been shown to lead to superior performance of n-channel MODFETs.@footnote 1@ Alternatively, the growth rates in LEPECVD can be lowered in order to allow for the synthesis of active channels with abrupt interfaces by this technique alone. Examples will be shown with strained Ge-rich channels up to 100 % Ge on relaxed buffers with Ge end concentrations between 50 and 70 %. Such structures have given rise to p-MOSFETs with effective hole mobilities exceeding the one of standard Si p-MOSFETs by up to a factor of four @footnote 2@. @FootnoteText@ @footnote 1@ T. Hackbarth et al., 11@super th@ European Workshop on Molecular Beam Epitaxy, Hinterzarten, Germany, 02/06/01. @footnote 2@ G. Höck et al., Appl. Phys. Lett. 76, 3920 (2000).

2:40pm **EL-WeA3 Self-Limited Layer-by-Layer Growth of Si by Alternated SiH@sub4@ Supply and Ar Plasma Exposure*, D. Muto***, *T. Seino, T. Matsuura, J. Murota,* Tohoku University, Japan

Self-limited layer-by-layer growth of Si without substrate heating has been investigated using ECR plasma. First, 5Å-thick epitaxial Si films on Si(100) were continuously deposited by Ar plasma with SiH@sub4@ at the Ar pressure of 16mTorr and the SiH@sub4@ partial pressure of 0.02mTorr with the microwave power of 800W. Then, by alternated SiH@sub4@ supply for 2min at the pressure of 10mTorr and the Ar plasma exposure for 5 or 20 sec at the pressure of 16mTorr with the microwave power of 200W, atomic-order Si epitaxial growth was carried out. The deposited Si films thickness was determined by AFM. Surface structure and hydrogen termination on the Si surface were evaluated by RHEED and FTIR/RAS, respectively. For the alternated process on the wet-treated surface, the Si deposition was scarcely observed on the wet-treated surface by the alternated process. By the continuous deposition, the wet-treated surface changed the dimer monohydride structure. As a result, the deposition rate was 0.3Å/cycle when the Ar plasma exposure time was 5sec. In this deposition cycle, the intensity of the dimer monohydride after SiH@sub4@ exposure was about 2/3 as that after Ar plasma exposure. When the Ar plasma exposure time increased to 20sec, the deposition rate was 0.5Å/cycle. The intensity of dimer monohydride was higher than that of 5sec Ar plasma exposure. These results mean that SiH@sub4@ molecule is adsorbed on the dimer monohydride structure, next Si epitaxial growth with the generation of the dimer monohydride structure is performed due to decomposition of adsorbed SiH@sub4@ by Ar plasma exposure. In conclusion, atomic-order layer-by-layer epitaxial growth of Si is achieved by SiH@sub4@ self-limited adsorption and enhanced reaction due to Ar plasma exposure.

3:00pm **EL-WeA4 Detrimental Effects in using Surfactant Assisted Growth*, G.G. Jernigan,*** U.S. Naval Research Laboratory, US*; P.E. Thompson, M. Fatemi, M.E. Twigg,* U.S. Naval Research Laboratory

Using STM, XPS, TEM, and XRD, we have investigated the use of Sb as a surfactant for the growth of SiGe quantum wells (QW) by molecular beam epitaxy. Our XPS results indicated that Ge surface segregation was inhibited from a Si capping layer after the growth of the QW with the use of an Sb surfactant, but Ge segregation during the growth of the QW was only partially prevented by the Sb surfactant. The differing effect Sb had on the start and the end of the growth of a SiGe QW led us to believe that something additional to the suppression of Ge segregation was occurring. An XRD analysis of many QW samples showed that Sb did not relieve strain in the SiGe QW but resulted in broader diffraction peaks due to compositional fluctuations within the QW. In agreement with the XRD, TEM showed that there was a greater amount of strain contrast within the QW due to compositional fluctuations. We will report our most recent results, using an in situ STM, which shows that Sb surfactant assisted growth has the detrimental effect of roughening the Si and SiGe surface while making the interface more compositionally abrupt.

3:20pm **EL-WeA5 Optical and Structural Characterization of GaN Films Grown by Molecular Beam Epitaxy on SiC Coated Si Substrates*, M. Lopez-Lopez***, *M. Cervantes-Contreras, M. Melendez-Lira, M. Tamura,* CINVESTAV-IPN, Mexico

High-quality GaN layers are difficult to grow on Si substrates due to the large lattice mismatch (17%), and the problems associated to the growth of a polar material on a non-polar substrate. MBE growth of GaN directly on Si frequently results in films with a mixture of the stable hexagonal phase and the metastable cubic phase. Single-crystal cubic GaN films can be obtained by coating the Si substrates with a thin SiC layer.@footnote 1@ Here we present a study of the effects of the orientation of SiC-coated Si substrates on the MBE growth of GaN. The GaN layers were grown in a conventional MBE system with an RF activated nitrogen plasma source. (100)- and (111) oriented Si substrates were chemical treated in a HF solution, and then annealed in the MBE preparation chamber under a C@sub 2@H@sub 2@ partial pressure. This resulted in the formation of ~2.5 nm-thick SiC epitaxial layer. Transmission electron microscopy and x-ray diffraction results showed that the growth on SiC-coated Si(100) leads to cubic GaN films, the growth on SiC-coated Si(111) resulted in predominantly hexagonal GaN. 12K-photoluminescence spectroscopy (PL) of the films on (100) substrates showed an intense emission at ~3.1 eV associated to a donor-acceptor pair transition. However, the PL spectra of films on (111) substrates showed an additional peak at ~2.4 eV, which could be associated to crystal defects. 300K-photoreflectance (PR) spectra presented transitions at ~3.2 and ~3.4 eV for GaN on (100)- and (111) Si substrates, respectively. A quantitative analysis of the PR line spectra was carried out using the third-derivative function theory. We obtained band-gap energy values lower than those generally accepted. These red shifts could be associated to residual tensile strain in the epilayers due to the lattice mismatch and the difference in thermal expansion coefficients between GaN and the Si substrate. @FootnoteText@ @footnote 1@ Y. Hiroyama and M. Tamura: Jpn. J. Appl. Phys. 37 (1998) L630.

3:40pm **EL-WeA6 Detailed Modeling of Si Gas-source MBE: Descriptions on Growth Rate and Hydrogen Coverage*, T. Murata***, *M. Suemitsu,* Tohoku University, Japan

In response to recent requirements from CMOS technologies, Si CVD is attracting renewed attentions. The attentions include needs for more complete understanding of the growth kinetics and a precise modeling of the growth. We here present the results of our growth experiments and a growth model based on the results. What is unique in our experiments is the observation of the surface hydrogen coverage @theta@ during growth, which is doubtlessly a key parameter in the description of the growth in CVD mode and yet has been quite rarely obtained in the past. To obtain @theta@ we employed Si gas-source molecular beam epitaxy using disilane, and have conducted temperature-programmed-desorption measurements on the surface quenched from the growth. Growth rate and @theta@ were obtained as a function of both the growth temperature and the source-gas pressure. We then tested two growth models based on the results. While the conventional 2-site-adsorption model well described the temperature- and the pressure-dependence of the growth rate, it failed to reproduce the behavior of @theta@. In contrast, the 2-site/4-site adsorption model developed previously by the authors@footnote 1@ showed almost complete fits to both the growth rate and the hydrogen coverage. The model assumes the 2-site and 4-site adsorptions to dominate the growth at low and high temperatures, respectively, and the present results prove its excellent ability to describe the Si growth in CVD mode. This work was supported in part by a Grant-in-aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology, Japan. @FootnoteText@ @footnote 1@ Suemitsu et al., Jpn. J. Appl. Phys. 36(1997) L625. .

4:00pm **EL-WeA7 Growth and Doping Kinetics in Si Gas-source MBE with In-situ Phosphrous-doping*, M. Suemitsu*,** *Y. Tsukidate,* Tohoku University, Japan

Being free of ion damages and redistribution of dopants during post-anneals in ion implantation, in-situ doped epitaxy is attracting renewed attention in ULSI processings. Remaining barriers are found mostly in N-type doping, where addition of PH@sub 3@ exhibits notable retardation of the growth and yet difficulties in achieving demanded high doping levels. In the studies presented here, we have experimentally and theoretically investigated the growth and doping kinetics in Si gas-source MBE using SiH@sub 4@ and PH@sub 3@. Experimentally, the growth rate (R@sub g@) and, more importantly, the hydrogen (H) and phosphorous (P) coverages on the growing surface were obtained by temperature-programmed desorption. The R@sub g@ Arrhenius plot showed a seemingly conventional separation into a high- and a low-temperature (LT) region with a low and a high activation energy, respectively, but obtained P and H coverages indicate that the domain I (550<T<650C) in the LT region is rate-limited solely by P@sub 2@ desorption while the domain II (T<550C) by both P@sub 2@ and H@sub 2@ desorptions. In domain I, the P coverage amounted to ~0.3 ML, some three orders of magnitude as high as in the bulk. This indicates a very rapid surface segregation of P atoms during growth, as well as its major role in impeding high doping levels. Surprisingly, mild PH@sub 3@ addition (<10ppm) in the high-temperature region were found to accelerate the growth rate. With the known site-blocking effects of P atoms[1], this suggests enhanced stickng probability of silane molecules at Si sites in the presence of surface P atoms. Based on these exprimental results, a theoretical model for growth/doping has been constructed and compared with experimental R@SUB g@ and P and H coverages.

4:40pm **EL-WeA9 Improved Surface Preparation for High Quality Homoepitaxial Growth of SiC*, W.V. Lampert*,** *C.J. Eiting, S.A. Smith, L. Grazulis, J.S. Solomon, T.W. Haas,* Air Force Research Laboratory, Materials and Manufacturing Directorate

Surface quality is a key factor in determining the quality of films grown by molecular beam epitaxy (MBE). Fullerene (C @sub 60@) and silicon (Si) effusion cells were used to grow superior quality homoepitaxial 6H-SiC. Prior to ex-situ processing, the wafers used for this study had the scratched surfaces and subsurface damage typical of commercial SiC wafers. Our ex-situ surface preparation includes chemical-mechanical polishing (CMP), carbon dioxide (CO @sub 2@) cleaning, hydrogen fluoride (HF) etching, de-ionized (DI) water rinsing, and nitrogen gas drying. Various surface analysis tools, such as Auger electron spectroscopy (AES) and atomic force microscopy (AFM), have been used to characterize the effects of these ex-situ processing steps. The results show that while our CMP processing adds surface contamination, it also leaves a scratch-free and stepped surface that is much more suitable for epitaxial growth. The results further show that the HF etching process step removes the contaminants left by the CMP process step and does not adversely effect the stepped surface. Results of these measurements and their implications for successful growth are discussed.

5:00pm **EL-WeA10 Initial Stages of Al@sub x@Se@sub y@ Heteroepitaxial Growth on Si(111)*, J.A. Adams*,** *A.A. Bostwick,* University of Washington*; E. Rotenberg,* Advanced Light Source, Berkeley*; F.S. Ohuchi, M.A. Olmstead,* University of Washington

Aluminum selenide is a largely unstudied material with interesting possibilities as a wide band gap semiconductor. Bulk Al@sub 2@Se@sub 3@ has a 3.1 eV band gap, and its hexagonal lattice constant (defected wurtzite structure) is about 1.3% larger than Si(111). However, very little is known about the properties of Al@sub x@Se@sub y@ heteroepitaxial films. Unlike Ga@sub x@Se@sub y@, which is stable in both layered GaSe and defected zincblende Ga@sub 2@Se@sub 3@ structures, layered AlSe has not been reported in either bulk or thin film form. We have used an Al@sub 2@Se@sub 3@ evaporative source to deposit thin films of Al@sub x@Se@sub y@ on Si(111) by molecular beam epitaxy. We investigated their electronic and atomic structure using angle-resolved valence band and core-level spectroscopy and diffraction, and compare these results to our previous work on Ga@sub x@Se@sub y@/Si(111). The initial Al@sub x@Se@sub y@/Si interface appears to form a bilayer structure similar to GaSe-terminated Si, although the temperatures for bilayer formation and for Se-evaporation from the film are higher for AlSe than for GaSe. Surface states (resonances) are well within the bulk Si bands, at least 1.2 eV below the Fermi level at the zone center. Despite the initial lone-pair termination, subsequent growth leads to photoelectron diffraction forward-focussing peaks along directions expected for the covalently-bonded wurtzite structure and not for layered AlSe.

Magnetic Recording Topical Conference
Room 110 - Session MR+AS+SE-WeA

Magnetic Recording: Heads & Media

Moderator: D. Weller, Seagate Technology

2:00pm **MR+AS+SE-WeA1 Ultra-Thin Magnetic Media Overcoats through ECR Deposition*, M.L. Wu*,** *J. Kiely, Y.T. Hsia, K.J. Howard,* Seagate Research

With increasing demands made on the performance of ultra-thin (<3 nm) overcoats in magnetic recording media, novel deposition approaches are needed to produce films that are mechanically robust and provide corrosion resistance to the underlying media. We have used the ECR (electron cyclotron resonance) approach to create a high-density plasma and have controlled the ion energy via the bias to increase the atomic mobility and density of deposited films. Using this approach, we have deposited a series of a-C:H (N) films with thicknesses as small as 0.8 nm and correlate their corrosion, wear, and nanometer-scale scratch resistance performance with film density measurements. We also present findings that the interaction with the cobalt underlayer changes with the ECR approach. The oxidation state of the cobalt underlayer was investigated by high resolution ESCA and preliminary results showed that the percentage of cobalt oxide was significantly decreased by the ECR approach while the C (1s) spectra showed the formation of cobalt carbide at the interface. We will contrast the behavior of films deposited with this approach with those conventional sputtered a-C:H (N) films, and comment on the extendibility of traditional overcoat designs.

2:40pm **MR+AS+SE-WeA3 Future Directions in Magnetic Storage Technology*, M.H. Kryder*,** Seagate Research **INVITED**

Magnetic recording technology has advanced in areal density by over 10 million times, since it was first introduced in disk drives in 1957. Recently, the rate of progress in areal density has exceeded 100% per year, far outstripping the pace of Moore's Law for semiconductor technology. Throughout this history there have been a number of innovations that have been made to enable the sustained progress. Today, however, we are approaching areal densities where a change in the form of the recording technology may be required. Longitudinal recording, which has been practiced in disk drives since 1957, is approaching densities at which recordings may become thermally unstable. This is forcing the industry to change the way disk drives are scaled and to consider alternative means of data storage. Technologies such as perpendicular recording, patterned media recording, optically assisted magnetic recording and probe storage are being considered. This talk will describe the methods that are being considered to extend longitudinal recording, the alternative technologies and their prospects for success.

3:20pm **MR+AS+SE-WeA5 Antiferromagnetically-Coupled Magnetic Media Layers for Thermally-Stable High-Density Recording*, E.E. Fullerton*,** *D.T. Margulies, M. Schabes,* IBM Almaden Research Center*; M.F. Doerner,* IBM Storage Technology Division **INVITED**

The combination of signal-to-noise requirements, write field limitations, and thermal activation of small particles is thought to limit the potential areal density of longitudinal recording media and is commonly referred to as the 'superparamagnetic limit'. Recording media composed of antiferromagnetically coupled (AFC) magnetic recording layers is a promising approach to extend areal densities of longitudinal media beyond these perceived limits [@footnote 1@,@footnote 2@]. The recording medium is made up of two ferromagnetic recording layer separated by a nonmagnetic layer whose thickness is tuned to couple the layers antiferromagnetically. For such a structure, the effective areal moment density (Mrt) of the composite structure is given by the difference between the ferromagnetic layers allowing the effective magnetic thickness to scale independently of the physical thickness of the media. This allows AFC media to maintain thermal stability even for low Mrt values. Experimental realization of this concept using CoPtCrB alloy layers that demonstrates thermally stable low-Mrt media suitable for high-density recording will be discussed. @FootnoteText@ @footnote 1@ E. E. Fullerton et al, Appl. Phys. Lett. 77, 3806 (2000). @footnote 2@ E. N. Abarra et al, Appl. Phys. Lett. 77, 2581 (2000).

4:00pm **MR+AS+SE-WeA7 Optimization of Media Properties in Magnetic Thin Films***, **E.B. Svedberg**[1], J.M. van de Veerdonk, K.J. Howard,* Seagate Research*; L.D. Madsen,* Carnegie Mellon University

Film depositions by ultra high vacuum magnetron sputtering with controlled gradients across the wafer in terms of composition and thickness have allowed (i) efficient exploration of a large number of variables, and (ii) the interdependencies between parameters to be studied. Output parameters such as coercivity and squareness of magnetic loops for magnetic media were measured and subsequently models were extracted that incorporated both the dependencies and co-dependencies of the input parameters. An added bonus to this approach is the tight control maintained on the "fixed" parameters (e.g. temperature and background pressure) through making many samples in a single deposition. To achieve the gradients, six tilted magnetrons were used to deposit the films. In one experimental setup the effect of underlayers was studied. The samples consisted of a set of layers as follows: Ta, RuxCo1-x, CoCr, CoCrPtB. In this setup, there seems to be an optimum Ru concentration in the range of 80-85% for achieving a maximum squareness, while the coercivity increases monotonically with the Ru concentration, hence, is not possible to maximize both the coercivity and the squareness in the same disc in terms of data. In a second set of samples the effort was focused on the hard magnetic layer and investigating the effect of the additives Ta, Nb, Pt and Ti to the CoCr to promote the desired magnetic properties. From the experiments it seems that the combination of Pt and Ta/Ti additives promotes a different growth mode than Pt or the additives alone. Further, to verify the possibility of structural characterization automation, two CoCr/Pt multilayers consisting of ten bi-layers each were mapped by x-ray diffraction. In the samples, the thickness of each Pt layer was kept constant over the surface of the wafer and the thickness of the CoCr layer was varied along with the total thickness.

4:20pm **MR+AS+SE-WeA8 Magnetic Nanoparticles and Nanoparticle Assemblies***, **S. Sun,*** IBM Research **INVITED**

We present our chemical synthetic approaches to monodisperse magnetic nanoparticles (Co and FePt) and nanoparticle superlattices. Advances of magnetic recording technology have driven the development of new magnetic nanoparticle-based media with uniformity in both particle size and particle magnetics. Self-assembly of magnetic nanoparticles may offer an easy way of fabricating such media. The key step for successful self-assembly approach is to use structurally stabilized magnetic nanoparticles as building blocks to form uniform nanoparticle arrays. We have found that steric repulsion from long chain hydrocarbon surfactants is effective in particle stabilization process. A combination of surfactants such as trialkylphosphine/oleic acid (for Co) and oleic acid/oleyl amine (for FePt) has been successfully employed to control particle growth, stabilize the particles, and protect them from oxidation. The particles can be prepared by metal salt reduction and metal carbonyl decomposition. By varying metal/surfactant or metal/metal ratio, both particle size (2-11nm) and alloy composition can be tuned. These monodisperse magnetic nanoparticles can self-organize into regularly arrayed magnetic superlattices. Microscopic studies of the assemblies have shown that the symmetry of these assemblies is dependent upon many factors including particle's size and shape. Thermal annealing is applied to adjust interparticle spacing of the superlattice assemblies and to control internal particle structure. Magnetic properties of these assemblies can be easily tuned from superparamagnetic to ferromagnetic. These well-controlled magnetic nanoparticle assemblies are of interest for future fabrication of nanoelectronic devices, and will have great potential for ultra-high density magnetic recording.

5:00pm **MR+AS+SE-WeA10 Thermal Stability of Granular Perpendicular Magnetic Islands Patterned using a Focused Ion Beam***, **S. Anders**, C.T. Rettner, M.E. Best, B.D. Terris,* IBM Almaden Research Center

We have studied the thermal stability of patterned magnetic media islands as a function of island size. A focused ion beam (30 keV, Ga+) was used to pattern granular CoCrPt media to produce square arrays of islands of different periods, ranging from 70-750 nm. Islands with periods smaller than 130 nm appear as single magnetic domains in MFM images, while larger islands show multi-domain behavior. The samples were magnetized perpendicularly in a field of 20 kOe (far in excess of the ~3 kOe coercivity) to produce fully magnetized films. This fully magnetized state should have the highest decay rate, since the demagnetization field is maximized. Magnetic force microscopy images taken at various times after the magnetization show that the patterned structures have a considerably slower thermal decay rate than the unpatterned film. Small single-domain islands were seen to have the smallest decay rate of less than 0.25% per decade compared to one order of magnitude higher decay rates for the unpatterned media. This enhanced stability is analyzed in terms of increased demagnetization fields and increased switching volumes introduced by patterning.

Nanometer Structures
Room 133 - Session NS+EL-WeA
Molecular Electronics and Patterning

Moderator: D.A. Bonnell, University of Pennsylvania

2:00pm **NS+EL-WeA1 Molecular Electronics by the Numbers***, **S.T. Pantelides,*** Vanderbilt University*; M. Di Ventra,* Virginia Tech*; N.D. Lang,* IBM **INVITED**

The paper gives an overview of recent work by the authors on first-principles, parameter-free calculations of electronic transport in molecules in the context of experimental measurements of current-voltage (I-V) characteristics of several molecules by Reed et al. The results show that the shape of I-V characteristics is determined by the electronic structure of the molecule in the presence of the external voltage whereas the absolute magnitude of the current is determined by the chemistry of individual atoms at the contacts. A three-terminal device has been modeled, showing gain. Finally, recent data that show large negative differential resistance and a peak that shifts substantially as a function of temperature have been accounted for.

2:40pm **NS+EL-WeA3 Controlled p-Doping of an Organic Molecular Semiconductor***, **W. Gao**, C. Chan, A. Kahn,* Princeton University

Electrical doping is perceived as the key to enhance the performance and versatility of organic molecular devices.@footnote 1@ Yet, few systematic investigations of the electronic structure of molecular films and interfaces doped with organic molecules have been published to date. We report here an investigation of controlled doping of zinc phthalocyanine (ZnPc) co-evaporated on Au with a strong acceptor, tetrafluoro-tetracyano-quinodimethane (F@sub 4@-TCNQ), using ultraviolet photoelectron spectroscopy (UPS) and inverse photoelectron spectroscopy (IPES). The 5.2 eV ionization energy of ZnPc is smaller than the electron affinity of F@sub 4@-TCNQ, suggesting host HOMO-to-guest LUMO charge transfer. Undoped ZnPc exhibits near mid-gap Fermi level (E@sub F@) and flat bands away from the Au interface, indicative of quasi-intrinsic purity. In ZnPc doped with ~3% (molar ratio) F@sub 4@-TCNQ, E@sub F@ shifts toward the HOMO level by 0.72eV and reaches ~ 0.16 eV above the leading edge of ZnPc HOMO, as measured from the surface of a 100Å film. At the interface with Au, the ZnPc HOMO is 0.72 eV below E@sub F@, leading to a depletion region with a 0.56eV band bending away from the interface, consistent with the p-type character of the film. The width of the depletion region in doped ZnPc is measured at approximately 32Å, consistent with a simple electrostatic model based on the doping concentration and a dielectric constant @epsilon@=3. The interface dipole barrier between Au and doped ZnPc is of the same sign and similar magnitude as for the undoped material. No evidence of chemical interaction can been seen, suggesting that pure charge transfer is the more likely mechanism for doping. The narrow depletion region in the doped layer is likely to lead to an increase in the tunneling of holes through the junction. I-V measurements will be performed to confirm this point. @FootnoteText@ * Work supported by the NSF (DMR-0097133) @footnote 1@Zhou et al., Appl. Phys. Lett., 78, 410 (2001).

3:00pm **NS+EL-WeA4 Conductance Switching in Single Molecules Through Conformational Changes***, **K.F. Kelly**, Z.J. Donhauser, B.A. Mantooth, L.A. Bumm, J.D. Monnell, J.J. Stapleton,* Penn State University*; D.W. Price,* Rice University*; D.L. Allara,* Penn State University*; J.M. Tour,* Rice University*; P.S. Weiss,* Penn State University

The viability of molecular electronics is being investigated with the aim of creating inexpensive, ultra-dense, high-capacity electronic devices. Conjugated phenylene-ethynylene oligomers have been extensively studied as candidate molecular devices. However, most experiments have required the assembly and study of these molecules in groups of thousands. We utilize self-assembly techniques in combination with scanning tunneling microscopy (STM) to study candidate molecular switches individually and in small bundles. Alkanethiol self-assembled monolayers (SAMs) on gold are used as a host two-dimensional matrix to isolate and to insulate electrically the molecular switches. The candidate molecules selectively adsorb into

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[1] **IUVSTA Welch Scholar**

existing defect sites and at step edges. The molecules bind with a sulfur "alligator clip" to the underlying gold substrate, and the ordered SAM causes the molecules to adsorb nearly normal to the substrate. We then individually address and electronically probe each molecule using STM. The conjugated molecules exhibit reversible conductance switching, manifested as a change in the apparent height in STM images. The observed switching occurs randomly and reversibly, with persistence times for each state ranging from seconds (or less) to hours. Both individual molecules and bundles of molecules exhibit switching. We have demonstrated the ability to control the amount and rate of active switching by controlling the local environment of the guest molecules. Inserting the guest molecules into poorly ordered matrix films results in increased switching activity when compared to well-ordered films. Similarly, annealing the SAM after inserting the guest molecules results in decreased switching activity, when compared to unannealed SAMs. We ascribe the switching to conformational changes of the molecules that are either enhanced or reduced by the corresponding loosening or tightening of the surrounding matrix.

3:20pm **NS+EL-WeA5 Epitaxial Growth of Self-Assembled Dots and Wires***,* ***S. Williams****,* Hewlett-Packard Laboratories **INVITED**

Various structures with nanometer-scale dimensions can be grown on surfaces by taking advantage of lattice mismatch, crystal symmetry and surfactant species. This provides experimentalists with an array of control parameters to tune the size and shapes of the structures that form. The general principals for attaining this control will be illustrated for various types of Ge nano-islands on Si(001) and also for nano-wires of various silicides on Si(001).

4:00pm **NS+EL-WeA7 Micro and Nanoscale Patterning of SAMs and Their Functionalisation***,* ***S. Sun****, K. Chong, G.J. Leggett,* University of Manchester Institute of Science and Technology, UK

Lithography methods are at the heart of modern-day microfabrication, nanotechnology and molecular electronics. These methods always rely on patterning of a resistive film followed by a chemical etching of the substrates. Self-assembled-monolayers (SAMs) of alkanethiols on metals (Au, Ag or Cu) have been found to be good resists to protect underneath metals from wet etching. In addition, due to the chemical reactivity of some groups on SAMs, various kind of materials can be immobilized onto it. Therefore patterning and functionalisation of SAMs have attracted great interest since the last decade. Various methods have been employed for this purpose. Here we report experiments that generate micro- and nanometer size patterns of SAMs. Micrometer size features have been obtained through masked photo-oxidation either by a high-pressure mercury arc lamp or a lamp that only emits 254 nm light. Proteins have been immobilised onto these features successfully and can exhibit both a lateral force and topography contrast. Nanometer scale patterns have been achieved by scanning alkanethiol coated atomic force microscope (AFM) tips across Ag/Au film surface, a method called dipped-pen-nanolithography (DPN). It has been found the transportation rate of alkanethiols from AFM tip to metal surface not only depend strongly on the humidity of the environment, but also on the quantity of alkanethiol adsorbed on the tip and properties of substrate of interest. Different feature sizes from several micrometers to less than 50 nm have been obtained by controlling the scan speed and the environment humidity. Similar with the SAMs on Au, the SAMs on Ag formed by this method can also be used as resist layer to protect underneath Ag film from chemical wet etching.

4:20pm **NS+EL-WeA8 Diffusion of Alkanethiols in the Presence of Water***,* ***P.E. Sheehan****, M.L. Stevens, L.J. Whitman,* Naval Research Laboratory

The patterning of alkanethiols has become a cornerstone in the burgeoning field of nanotechnology. Several patterning techniques have been developed, the more popular of which include stamping using polymer masters, known as microcontact printing (mCP) and, more recently, the direct writing of the thiols using an AFM tip, known as Dip Pen Nanolithography (DPN). Importantly, in both techniques, diffusion of the thiol away from the contact area fundamentally limits the spatial resolution obtained. Obtaining the highest resolution possible from these techniques will require a full understanding of the rate and nature of thiol diffusion. To address this need, the radii of octadecanethiol spots deposited via DPN were studied as a function of tip-surface contact time and relative humidity. The increase in spot size with time was well described by two-dimensional radial diffusion from a constant source of finite radius. Fits using this formula revealed a diffusion constant of approximately 2500 nm2/sec with little dependence on humidity. Analysis of published images@footnote 1@ showing the spread of hexadecanethiol on gold after microcontact printing leads to comparable diffusion constants. Significantly, these values are four orders of magnitude smaller than that expected for diffusion through bulk water. Mechanisms that would explain such a low diffusion coefficient will be discussed. @FootnoteText@ @footnote 1@ Y. Xia and G.M. Whitesides, J. Am. Chem. Soc. 117 (1995) 3274.

4:40pm **NS+EL-WeA9 Chemical Nanolithography***,* ***A. Gölzhäuser****, W. Geyer, A. Küller, V. Stadler, W. Eck, M. Grunze,* Universität Heidelberg, Germany*; T. Weimann, P. Hinze,* Physikalisch Technische Bundesanstalt, Germany*; K. Edinger,* University of Maryland

The efficient fabrication of chemically defined surface nanostructures is an important objective in fields such as molecular electronics, biochips or biosensors. Chemical nanolithography utilizes electron beams to selectively modify self-assembled monolayers, for example to convert NO@sub 2@ end groups in monolayers of nitrobiphenylthiol to NH@sub 2@ groups.@footnote 1,2@ In this presentation, we show that chemical nanolithography can fabricate chemical features with lateral dimensions down to ~20 nm on a variety of different surfaces (noble metals, semiconductors or oxides). E-beam lithography as well as low energy electron proximity printing are used to fabricate chemical surface structures. These are then used as high resolution templates for the laterally controlled electrochemical deposition and for the immobilization of molecules (or macromolecular objects) on predefined surface regions. @FootnoteText@ @footnote 1@ W. Eck, V. Stadler, W. Geyer, M. Zharnikov, A. Gölzhäuser, M. Grunze, Adv. Mater. 12, 805 (2000). @footnote 2@ A. Gölzhäuser, W. Eck, W. Geyer, V. Stadler, T. Weimann, P. Hinze, M. Grunze, Adv. Mater. in press.

Organic Films and Devices
Room 131 - Session OF+TF+EL-WeA

Growth of Organic Thin Films

Moderator: T. Fritz, TU Dresden, Germany

2:20pm **OF+TF+EL-WeA2 Resonant Mid-Infrared Pulsed Laser Deposition of Polymer Films***,* ***R.F. Haglund****, M.R. Papantonakis,* Vanderbilt University*; D.M. Bubb, J.S. Horwitz, J.S. Callahan, R.A. McGill, E.J. Houser, D.B. Chrisey,* Naval Research Laboratory*; M. Galicia, A. Vertes,* George Washington University*; B. Toftmann,* Risoe National Laboratory, Denmark

Resonant, picosecond-pulse, mid-infrared laser irradiation has been shown to ablate glassy and crystalline solids with high efficiency and low collateral damage.@footnote 1@ We have extended this concept to show that resonant infrared (IR) pulsed-laser deposition (PLD) is an effective method for depositing polymer films with physical and chemical structure as well as optical properties virtually identical to those of the bulk starting material. This contrasts sharply with PLD at ultraviolet (UV) wavelengths, where deposited polymer material is sometimes significantly degraded. In our experiments, the organic starting material was ablated by a pulsed infrared, free electron laser tuned into resonance with various vibrational modes; the vapor was collected on a room-temperature substrate. For polyethylene glycol (PEG, MW 1450) the laser was tuned to either C-H or O-H stretching modes at 2.9 and 3.4 µm, respectively. The properties of the deposited film were determined using infrared absorption spectroscopy and mass spectrometry. When the infrared laser was detuned from resonance, the structure and optical properties of the deposited PEG film were significantly altered, showing that the off-resonance ablation process thermally damages the polymer. The potential for generalizing this technique can be seen in the successful deposition of poly(lactide co-glocolide) (PLCA, MW 67,000). PLCA films were deposited using 5.7 µm excitation (1754 cm@super-1@), where the laser excitation is localized by the C=O stretch. The mechanism of ablation appears to be explosive vaporization; in contrast to the photochemical mechanism typical of UV ablation, the ablated material seems to remain in the electronic ground state. The technique appears promising for biomedical and electronic applications of polymeric and organic thin films. @FootnoteText@ @footnote 1@ D. R. Ermer, M. R. Papantonakis, M. Baltz-Knorr, D. Nakazawa and R. F. Haglund, Jr., Appl. Phys. A 70, 633-635 (2000).

2:40pm **OF+TF+EL-WeA3 Synthesizing Thin and Ultrathin Polymer Films by a Two-step Deposition/Polymerization Process***,* ***J. Bai****, C.M. Snively, W.N. Delgass, J. Lauterbach,* Purdue University

The goal of this work is to understand and further develop an in-situ preparation method for producing high quality polymer thin films. In this two-step vacuum process, a monomer film is deposited onto a cooled substrate, and then the polymerization reaction is initiated; thus the polymerization is confined to the substrate. Compared to other preparation techniques, this process has the major advantages of allowing the fabrication of films from insoluble polymers and providing better control of film quality. This investigation focused on the molecular orientation and packing of the monomer, as well as polymerization kinetics and film quality characterization. In-situ adsorption and polymerization studies were done using Reflection-Absorption Infrared Spectroscopy (RAIRS) and Temperature-Programmed Desorption (TPD). Time resolved FTIR spectra were taken to study the factors controlling the rate of polymerization. GPC, ellipsometry and AFM provided information about molecular weight, film thickness, and morphology characterization of the films. The model systems investigated were styrene and methyl methacrylate (MMA) on platinum. For the styrene/Pt model system, kinetic studies reveal that the polymerization reaction is preferred in amorphous monomer layers. Ellipsometry measurements show that, in the range of 25-200nm, the polystyrene film thickness is a linear function of the monomer dosage. AFM data suggest that the resulting film morphology is influenced by the platinum substrate. Polarized RAIRS spectra of MMA show that, up to 0.2 micron, only p-polarized component of the beam contributes to the spectrum, indicating that RAIRS can be used to determine the molecular orientation of films with sub-micron thickness.

3:00pm **OF+TF+EL-WeA4 Surface Growth Study of Pentacene, Perylene and CuPc***, **S. Zorba**, N.J. Watkins, L. Yan, Y. Gao,* University of Rochester

Pentacene, Perylene and CuPc are widely used organic semiconductors in organic light emitting diode (OLED) and organic thin film transistor (OTFT) applications. It has been well established that the transport properties of these materials are strongly dependent upon the way they are grown as organic thin films. One of the reasons why these materials are so popular is the fact that their electronic properties, such as their mobilities and barrier to charge injection ratios, can be altered and improved by changing their morphologies. In this talk we will present our recent results on the different growth modes of these substances on different substrates and try to relate their observed electronic and transport properties to their morphologies and account for their favorable features.

3:20pm **OF+TF+EL-WeA5 Substrate Controlled Crystallisation of Ultra-thin Films of Perylene***, **Q. Chen**, N.V. Richardson,* University of St Andrews, UK*; P.J. Unwin, T.S. Jones,* Imperial College of Science, Technology and Medicine, UK*; T. Rada, A.J. McDowall,* University of St Andrews, UK

There has been recent interest in the electronic and optoelectronic properties of polyaromatic hydrocarbons, such as tetracene, pentacene and perylene, because of their potential use as organic lasers, OLEDs and OFETs. Device performance is likely to be strongly influenced by the structural quality of crystals or thin films. We have carried out a detailed investigation of the deposition and growth of ultra-thin films (0-30 monolayers) of perylene on a variety of substrates including Cu{110}, H/Si(111), InAs(111) and InSb(111), using STM, TPD, LEED and vibrational spectroscopies. The substrate has a profound influence on growth and subsequent crystallinity of the film. For example, films grown on a hydrogen terminated Si(111) surface show no evidence of layer-by-layer growth and, from the earliest stages, small clusters of randomly oriented molecules are present which eventually cover the surface with a rough polycrystalline film. In contrast, vacuum deposition on a Cu{110} surface leads to large crystalline domains upto one monolayer coverage. Electron energy loss spectroscopy confirms that the molecules are flat-lying and @pi@-bonded to the substrate. Multilayer growth takes place epitaxially layer-by-layer on this first monolayer into a structure which, although commensurate with the underlying copper surface along the direction is incommensurate along and is unrelated to the bulk crystal structure of perylene. The 2D unit cell at all layer thicknesses (to 30 monolayers) is rectangular with dimensions 2nm x 1.9nm containing two, flat-lying molecules per layer at 90° to each other around an axis normal to the substrate surface. The molecular rows along are out-of-phase with each other in the direction from layer to layer, in an ABA packing sequence of rows along the growth direction. The implications for the modification of film properties implied by this control over film structure and crystallinity will be discussed.

3:40pm **OF+TF+EL-WeA6 Probing the Reactivity of Multifunctional Compounds on Semiconductor Surfaces: Pyrrole and its Derivatives on Si and Ge(100)-2x1***, **G.T. Wang**, C. Mui, C.B. Musgrave, S.F. Bent,* Stanford University

While the chemistry of amines has been extensively studied on the Si(100)-2x1 surface, relatively little is known about their reactivity with the Ge(100)-2x1 surface. In this study, the reactions of pyrrole and multiple pyrrole derivatives, including methylpyrrole, pyrrolidine, and methylpyrrolidine, with the Ge(100)-2x1 and Si(100)-2x1 surface were investigated via multiple internal reflection infrared spectroscopy and ab initio quantum chemistry calculations. This series of compounds comprises a model system for examining the competition of multiple functionalities on Ge(100) and Si(100) and the role kinetics and thermodynamics play on selectively controlling growth of organics on semiconductor surfaces. Although these compounds are structurally similar, they each follow different reaction mechanisms on the Si surface, including dative bonding, N-H dissociation, cycloaddition, and electrophilic aromatic substitution. We have also found that the adsorption of pyrrole and its derivatives on the Ge surface is surprisingly different from the Si surface. While the reaction of organics on Si is typically under kinetic control, the experimental and theoretical results show that thermodynamical considerations are also necessary to explain the reaction of organics on Ge. Additionally, aromaticity and charge transfer to the surface are found to have significant effects on the adsorption behavior of these compounds.

4:00pm **OF+TF+EL-WeA7 Chemisorption of Vinylacetic Acid on Si(001) and Its Subsequent Reaction with Iron Pentacarbonyl***, K. An, S.S. Lee, **Y. Kim**,* Korea Research Institute of Chemical Technology, South Korea

Chemisorption of vinylacetic acid (VAA) on clean Si(001) substrate at room temperature and the change of its adsorption with temperature have been investigated by x-ray and ultraviolet photoelectron spectroscopy. It was hoped that the C=C double bond of the chemisorbed VAA may be utilized in the subsequent reaction with the second adsorbate, iron pentacarbonyl, Fe(CO)@sub 5@, in this study. VAA first adsorbs on Si(001) molecularly, and as the substrate temperature is increased to 350°C, loses the acidic hydrogen resulting in the configuration that has two equivalent oxygen atoms according to the change in the O 1s XPS peak. The curve-fitted Si 2p peak indicates formation of the Si@super 2+@ state on the surface. UPS also showed that the photoemission peak due to the OH group of VAA loses its intensity significantly. This surface species is stable up to about 350°C. As the temperature is raised even more to ~450°C, the adspecies are decomposed leaving a mixture of oxidized silicon and silicon carbide. At about 700°C, only tenacious oxygens remain on the carbided substrate surface. Iron pentacarbonyl was introduced into the XPS analysis chamber to 35000 L with the monolayer of the anionic species of VAA at 350°C. The surface, after the introduction of Fe(CO)@sub 5@, was found to consist of the acid anion and an iron species that shows metallic behavior according to XPS and UPS data. The Fe(CO)@sub 5@ molecules must have been completely dissociated since no accumulation of C or O adspecies has been detected. Also the surface iron atoms do not seem to have been oxidized judging from the shape of the Fe 2p level and the appearance of the Fermi level crossing. However, it is not yet clear whether the iron species have formed microscopic structures or not, while the change in the C 1s peak suggests that they may each have a chemical bond with the surface C=C double bond. At the moment a scanning tunneling microscopy experiment is in preparation to examine the surface structure of the iron species.

4:20pm **OF+TF+EL-WeA8 Possibilities of Electron Beam Nanometer-scale Fabrication of Si(111) Using Alkyl Monolayers***, **T. Yamada**, N. Takano, K. Yamada, S. Yoshitomi, T. Inoue, T. Osaka,* Waseda University, Japan

Utilization of monolayer materials covering Si wafer surfaces is prospective in mass-production of nanometer-scale patterns generated by electron beam drawing, maintaining the spatial resolution. This paper presents application or monolayers of organic moieties bonded on Si(111) for electron-beam patterning and successive chemical metal deposition processes over the patterns. For the purpose of passivation and chemical alteration of Si(111) surface, alkyl groups were deposited by contacting H:Si(111)(1x1) with Grignard reagents (C@sub n@H@sub 2n+1@MgX, X=Cl, Br, I, as tetrahydrofuran solutions).@footnote 1@ Vibrational spectroscopy by FT-IR and HREELS indicated that the bonds in alkyl groups delivered as the Grignard reagent remained unbroken, and that most of the terminating H atoms were replaced by the alkyl groups. STM revealed the original step/terrace structure of Si(111) uniformly covered with a monolayer of organics. The alkyl groups were arranged in a rather disordered manner within the monolayer. Auger electron spectroscopy resulted that the number of alkyl groups per a unit area is constant with respect to the chain length n in the range of 1 ~ 18. All these facts indicate that the alkyl groups are covalently bonded to Si(111). Electron bombardment in vacuum did not introduce useful alteration of the adlayer, and patterning by electron beam (incident energy <3 kV) with ambient O@sub 2@ atmosphere (<10@super -6@ Torr) deposited SiOx on the irradiated portions. Metals such as Ni and Cu were deposited only over the patterns by immersion into aqueous solutions including metal ions. The electron beam patterns were even visualized as metal-deposited area limited by the passivation effect of alkyl monolayer. Application of this entire process to the patterns of <100 nm is now attempted to explore the spatial resolution limit on the nanometer scale. @FootnoteText@ @footnote 1@R. Boukherroub, S. Morin, F. Bensebaa and D. D. M. Wayner: Langmuir 15 (1999) 3831.

Plasma Science
Room 104 - Session PS-WeA
Plasma Surface Interactions II

Moderator: E.R. Fisher, Colorado State University

2:00pm **PS-WeA1 Laser Desorption-Laser Induced Fluorescence In situ Studies of Si Etching in Inductively-Coupled Cl@sub 2@-Ar Plasmas*, N.C.M. Fuller*[1]**, Columbia University*; V.M. Donnelly,* Agere Systems*; I.P. Herman,* Columbia University

Laser desorption-laser induced fluorescence (LD-LIF) is used to determine the surface coverage of chlorine during the steady-state etching of Si in an 18 mTorr inductively-coupled Cl@sub 2@-Ar plasma as a function of the rf power, substrate bias and Cl@sub 2@ fraction. Laser repetition rate studies, which indicate how the surface is re-chlorinated between laser pulses after each step of laser desorption of surface SiCl@sub x@, reveal that close to steady-state chlorination is achieved in the 10 ms time between 308-nm laser pulses (at 100 Hz) even with only 6% Cl@sub 2@ (94% Ar). This is not unexpected given our prior work in neat Cl@sub 2@ plasmas, for which there is near steady-state chlorination between such laser pulses at 1 mTorr pressure. A mechanism for the competitive etching processes of chlorination (mostly by Cl atoms in the bright mode) and surface sputtering (mostly by Ar and Cl positive ions) will be presented, by coupling these surface adlayer measurements with the etch rates and the optical emission actinometry determination of the densities of the major neutral and positive ions in the plasma.

2:20pm **PS-WeA2 Monitoring Plasma-Wall Interactions During Etching of Thin Film Stacks*, S.J. Ullal*[2]**, University of California, Santa Barbara*; H. Singh, J. Daugherty, V. Vahedi,* Lam Research Corporation*; E.S. Aydil,* University of California, Santa Barbara

Surface reactions on plasma etching reactor walls affect the species concentrations in the discharge and plasma properties such as electron temperature and ion flux. Despite the importance of plasma-wall interactions, reactions occurring on surfaces in contact with the plasma are poorly understood and wall conditions are uncontrolled during etching. Often, a stack of thin films of different materials must be etched sequentially in the same reactor using different gases. Complex multi-layered films are deposited on the chamber walls during the etching of the stack and interaction between successive etching steps through the changing wall conditions may have deleterious effects. Thus, it is critical to monitor the wall conditions and the nature of the films and adsorbates that are deposited on the walls. We have developed a surface probe based on in situ multiple total internal reflection Fourier transform infrared (MTIR-FTIR) spectroscopy as a diagnostic to monitor the films and adsorbates on the walls of an inductively coupled plasma etching reactor. Using this probe we studied the shallow trench isolation etching of Si where a photoresist patterned stack of anti-reflection coating, Si@sub 3@N@sub 4@, SiO@sub 2@ and Si is etched sequentially using gases as varied as fluorocarbons, Cl@sub 2@, HBr, and O@sub 2@. During the fluorocarbon etching of Si@sub 3@N@sub 4@ and SiO@sub 2@, fluorocarbon films deposit on the chamber walls. During the subsequent etching of Si by Cl@sub 2@/O@sub 2@, etch products such as SiCl@sub x@ react with the O in the plasma and deposit a silicon oxychloride layer on the reactor walls on top of the fluorocarbon layer. In order to maintain etching reproducibility, these multi-layered films must be cleaned before the next wafer is etched in the chamber. Reactions occurring on the wall surfaces and strategies to remove these complex multi-layered films to maintain reproducibility of wall conditions and etching processes will be discussed.

3:00pm **PS-WeA4 Controlling the Ion Flux and Energy Distributions in LAPPS@footnote 1@*, S.G. Walton*,** *D. Leonhardt, D.D. Blackwell, D.P. Murphy, R.F. Fernsler, R.A. Meger,* Naval Research Laboratory

In situ mass and energy resolved measurements of ion fluxes to a conducting electrode surface in NRL's Large Area Plasma Processing System (LAPPS) are presented. In LAPPS, a high-energy electron beam is used to ionize a background gas, producing a plasma over the volume of the beam. The beam is generated by a linear hollow cathode and magnetically collimated which allows for the production of uniform plasmas over areas up to 1 m@super 2@ or more. Electron beams are efficient at producing high-density plasmas (10@super 10@-10@super 12@ cm@super -3@) at low temperatures (Te < 1.0 eV) and are decoupled from the reactor geometry. Hence, control over the flux and incident ion energy at independently located and biased electrodes is possible and advantageous in dry processing applications. Temporally resolved ion flux and energy distributions at an electrode surface are reported for pulsed discharges in noble and molecular gases. The flux, sampled through a small orifice located in the center of the electrode, is analyzed via an energy selector in series with a mass spectrometer. Measurements are presented for a grounded and RF-biased electrode as a function of operating pressure, source-electrode separation, and the applied bias. In argon for example, the incident Ar@super +@ energy is pressure dependent and found to scale with the applied RF bias. In molecular gases, the magnitude and composition of the flux is dependent upon the source-electrode separation and found to vary in time, particularly in the afterglow. The results are discussed in terms of processing applications. Additional details concerning LAPPS are presented by co-authors at this conference.@footnote 2@ @FootnoteText@ @footnote 1@ Work supported by the Office of Naval Research @footnote 2@ See presentation by D. Leonhardt and D.D. Blackwell. @footnote *@S.G. Walton: SFA, Inc.; D.D. Blackwell: NRC Postdoctoral Research Associate

3:20pm **PS-WeA5 High-Density Plasma-Based Etching of Organosilicate Glass (OSG) in C@sub 4@F@sub 8@/Ar and C@sub 4@F@sub 8@/O@sub 2@ Gas Mixtures: Process Results and Diagnostics*, M. Fukasawa*,** *X. Li, X. Wang, L. Ling, G.S. Oehrlein,* University of Maryland, College Park*; F.G. Celii, K.H.R. Kirmse,* Texas Instruments, Inc.

We report gas phase and surface studies of high-density plasma etching processes of organosilicate glass (OSG), a low-k oxide, and Si@sub 3@N@sub 4@ and SiC etch stop materials, in C@sub 4@F@sub 8@/Ar and C@sub 4@F@sub 8@/O@sub 2@ gas mixtures. Owing to the presence of methyl groups in the SiO@sub 2@ backbone the etching behavior of OSG differs significantly from that of conventional SiO@sub 2@. The addition of O@sub 2@ can be used to increase the OSG etching rate (e.g. from 900 nm/min for a 1400 W 6 mTorr C@sub 4@F@sub 8@ discharge and a selfbias voltage of -85 V to 1100 nm/min for C@sub 4@F@sub 8@/20% O@sub 2@), but can modify the OSG material by oxidizing methyl groups and reduce the selectivity to the etch stop material. The goal of this work was to establish the key variables that can be used to maximize the etch selectivity of OSG with respect to the etch stop materials while minimizing the OSG modifications. An inductively coupled high-density plasma etching reactor equipped with in situ ellipsometry, optical emission spectroscopy (OES) and mass spectrometry was used. Measurements were made as a function of C@sub 4@F@sub 8@/Ar and C@sub 4@F@sub 8@/O@sub 2@ gas composition for pressures ranging from 6 to 20 mTorr, source power levels up to 1400 W, and as a function of RF bias. Both blanket film etching of OSG, SiO@sub 2@, Si@sub 3@N@sub 4@ and SiC and transfer of hole/trench patterns into OSG were studied as a function of process conditions. We utilized the gas phase characterization results, and X-ray photoelectron spectroscopy (XPS) data of etched films after vacuum transfer, to explain the observed etching behavior, evaluate surface/bulk modifications of the OSG vs. process conditions, and identify the critical factors that enable high quality pattern transfer processes of OSG over Si@sub 3@N@sub 4@ and SiC.

3:40pm **PS-WeA6 Plasma Deposition of Silicon Thin Films: Atomic-Scale Modeling of Radical-Surface Interactions*, D. Maroudas*,** University of California, Santa Barbara **INVITED**

Hydrogenated amorphous silicon (a-Si:H) thin films grown by plasma-assisted deposition from silane-containing discharges are used widely in technological applications. A fundamental understanding of the interactions of radicals, such as SiHx (0<x<4) and H, with the growth surface is required for the development of improved a-Si:H deposition strategies.

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[1] **PSTD Coburn-Winters Student Award Finalist**

[2] **PSTD Coburn-Winters Student Award Finalist**

Toward this goal, we have developed a hierarchical atomic-scale modeling approach for identification and analysis of the interactions between silane fragme nts and silicon growth surfaces and for systematic characterization of the computationally generated a-Si:H films. This approach combines classical molecular-dynamics (MD), molecular-statics, and Monte Carlo simulations with quantum mechanical calculation s of surface reaction energetics based on density functional theory. Our MD simulations of radical impingement on the growth surface reveal several classes of surface reactions that occur during amorphous film deposition and their role in the growth proce ss. Surface hydrogen is removed by abstraction reactions according to Eley-Rideal or Langmuir-Hinselwood mechanisms. Silicon is incorporated into the growing film through radical attachment to surface dangling bonds, as well as radical insertion into Si-Si surface bonds including dissociative adsorption reactions. In addition, reactions that involve Si-Si bond formation between adsorbed species are identified and analyzed. Various surface migration mechanisms for mobile surface species also are discussed. The simulated evolution of the film's structure, surface morphology and roughness, surface reactivity, and surface composition is analyzed systematically. Finally, our simulation results are compared with experimental measurements based on ATR-FTIR spectroscopy for the temperature dependence of the H coverage of the surface and surface hydride content. The comparisons are used to discuss our current understanding of the deposition mechanism.

4:20pm **PS-WeA8 Molecular Dynamics Simulations of Ar@super +@-Si and Si:F Interactions***, **D.B. Graves**, D. Humbird,* University of California at Berkeley

4:40pm **PS-WeA9 Atomic-Scale Simulation Study of the Role of H Atoms in the Amorphous to Nanocrystalline Transformation in Plasma-Deposited Silicon Thin Films***, **S. Sriraman**, E.S. Aydil, D. Maroudas,* University of California, Santa Barbara

Hydrogenated amorphous (a-Si:H) and nanocrystalline (nc-Si:H) silicon thin films grown by plasma deposition from SiH@sub 4@ and H@sub 2@ containing discharges are widely used in photovoltaic and flat-panel display technologies. When an a-Si:H thin film is exposed to a H@sub 2@ plasma, its nanostructure changes from amorphous to nanocrystalline. Though several hypotheses have been proposed, the fundamental mechanisms behind this transformation are still not well understood. Molecular dynamics (MD) simulations of the interactions of thermal and energetic H atoms with a-Si:H films and their surfaces are used to elucidate the nanoscopic mechanisms behind the amorphous to nanocrystalline transformation. a-Si:H films are deposited through MD simulations of repeated impingement of individual SiH@sub 3@ precursors on an initial H-terminated Si(001)-(2x1) surface. H@sub 2@ plasma exposure is simulated through repeated impingement of individual H atoms onto these a-Si:H films grown by MD. Of the many elementary surface reactions that were identified, Eley-Rideal type H abstraction reactions are believed to mediate strain relaxation processes and promote amorphous to nanocrystalline transformation. The effects of abstraction reactions on the growth surface are examined by analyzing their influence on both local and overall film structure. The surface hydride compositions in the deposited films before and after exposure are compared with experimental data and the comparisons are used to discuss our current understanding of the amorphous to nanocrystalline transformation.

5:00pm **PS-WeA10 A Fast Computational Model for Study of Coupled Bulk Plasma-Sheath-Bias Circuit Phenomena and its Effect on Plasma-Surface Interactions***, **L.L. Raja**,* Colorado School of Mines*; E. Meeks,* Reaction Design, Inc.

High-density plasma reactors are used extensively in the etching and deposition of thin films in the manufacture of large-scale integrated circuits. With feature sizes approaching 0.1 microns and lower, it is increasingly important to develop quantitative understanding of plasma-surface interactions and their dependence on plasma reactor geometry, operating conditions, and bias-circuit settings. Of critical importance is the relationship between reactor controls and ion impact phenomena such as the Ion Energy and Angular Distribution Functions (IEDF and IADF). We have developed a new fast computational software tool that enables prediction of IEDF and IADF in high-density plasma reactors through coupling of bulk plasma, RF sheath, and bias circuit models. We simulate the bulk plasma using the well mixed reactor model, AURORA,@footnote 1@ while the RF sheath sub-model uses a multiple-ion extension of the Riley sheath model@footnote 2,3@ coupled to a typical bias circuit model, based on first-principles. The coupled model handles detailed gas-phase chemical reactions that are characteristic of process plasmas and can predict multiple ion IEDFs and IADFs as a function of reactor geometry, and reactor and bias circuit settings. The general surface-chemistry capability allows for specification of ion-energy dependent yields for ion-enhanced surface reactions. The coupled model executes within minutes on a personal computer, providing a fast simulation tool for quickly exploring alternative process conditions and reactor designs. Example results in a fluorocarbon plasma etching system will be reported. @FootnoteText@ @footnote 1@R. J. Kee, F. M. Rupley, J. A. Miller, M. E. Coltrin, J. F. Grcar, E. Meeks, H. K. Moffat, A. E. Lutz, et al., Chemkin Collection 3.6, (Reaction Design, Inc., San Diego, CA, 2000) @footnote 2@M. E. Riley, Sandia National Laboratories Report No. SAND95-0775, 1995. @footnote 3@M. E. Riley, Sandia National Laboratories Report No. SAND96-1948, 1996.

Semiconductors
Room 111 - Session SC+SS+EL-WeA
Chemistry of Semiconductor Etching & Cleaning

Moderator: G. McGuire, MCNC

2:00pm **SC+SS+EL-WeA1 The Chemistry of Anisotropic Silicon Etching: Tackling an Old Problem with New Tricks***, **M.A. Hines**,* Cornell University **INVITED**

Aqueous bases, such as KOH, TMAH, and NH@sub 4@F, are the most important class of industrial silicon etchants. The popularity of these etchants is driven in large part by their extreme anisotropy (i.e. their high face-specificity). Relatively little is known about the chemical origins of etchant anisotropy, though. The problem is simple. On an atomic scale, an anisotropic etchant must be highly defect selective, but the study of surface defect reactivity is notoriously difficult. In this talk, I will discuss two new approaches to studying these reactions. On an atomic scale, I will show how defect reactivity can be quantified using a combination of scanning tunneling microscopy (STM) experiments and atomistic kinetic Monte Carlo simulations. This combination yields very detailed information about site-specific reactivity. To complement these rather time-consuming studies, I will also describe a new technique, which uses microfabricated test patterns, to rapidly assay the reactivity of 180 silicon surfaces simultaneously. We use this technique to perform orientation-resolved chemical kinetics experiments. I will show that the orientation-dependence provides additional insights into chemical reactivity. New phenomena, such as orientation-dependent morphological transitions, will also be described.

2:40pm **SC+SS+EL-WeA3 In situ Infrared Spectroscopy of Wet Chemical Etching of Si and InP with Electrochemical Control***, **O. Pluchery**, S.B. Christman, Y.J. Chabal,* Agere Systems

The fabrication of Integrated-Circuits requires many different steps, including growth or etching. Since device performance strongly depends on surface preparation and control at each step, we have developed in situ Fourier transform infrared (FTIR) spectroscopy using multiple internal reflections to monitor the nature of interfaces. At the heart of high speed silicon technology is the growth of ultra thin oxide layer on top of the Si substrate. We monitor here the structure of such thermally grown oxides by sequential etching in dilute HF. The analysis of the LO and TO vibrational phonon modes of the oxide at 1070 and 1270 cm@super -1@ respectively shows that the etching mechanism exhibits two kinetic regimes depending on whether the HF flow wets the surface in a static or dynamic way. For static wetting, the LO absorption of the oxide undergoes a dramatic distortion that can be related to the unusual nature of the diffuse layer in the vicinity of the oxide surface. The etching mechanism depends in effect on the competition between diffusion and kinetics in this layer. In contrast to silicon, the passivating oxides of InP substrates are rather intricate. We examine here InP wafers that are covered by a thin oxide typical of "epi-ready" wafers offered by vendors. Analysis of the FTIR spectra shows a coexistence of several phases, such In@sub 2@O@sub 3@ (850 cm@super -1@) and InPO@sub 4@ at higher frequencies along with mixed oxide phases at intermediate frequencies. These oxides can also be removed by etching in HCl (10 wt%). This leaves a clean but very reactive InP surface that quickly attracts contaminants so that in situ analysis is highly desirable. In addition to the in-situ spectroscopy, we have devised an electrochemical control of the surface that makes it possible to further modify the composition of the adlayer as well as the diffuse layer.

3:00pm **SC+SS+EL-WeA4 Atomic Hydrogen Etching in Hot Wire Chemical Vapor Deposition System of Silicon Thin Films*, O. Srivannavit,*** University of Michigan

Atomic hydrogen generated by the filament in Hot Wire Chemical Vapor Deposition System plays an important role in depositing of thin films. It is believed that the etching process by atomic hydrogen taking place during the deposition process is one of key mechanism to obtain high quality thin films. In order to see a clear effect of interaction of atomic hydrogen with the growth surface, we focused only on the etching process in this system. We used amorphous and crystalline silicon as the substrate and then monitored its etching rate. The etching rate increases with increases of filament temperature due to increasing amount of atomic hydrogen generated on the filament. When substrate temperature increases, the etching rate decreases. We believe this is due to the decrease of the surface coverage of hydrogen with the increase of substrate temperature. The etching rate increases initially with pressure increase and then remains constant with further pressure increase. This phenomenon indicates that there is the competition between the increase in the amount of the atomic hydrogen generated and decrease in the diffusion coefficient of atomic hydrogen to the etching surface when pressure increases. The etching rate increases in the order of amorphous Si > poly-Si > crystalline silicon. This effect plays a key role in the selective deposition in this system.@footnote 1@ In addition, we found that there is preferential crystalline orientation etching (111) < (110) < (100) which can be used to explain the crystalline orientation during deposition of poly-Si films in this system.@footnote 2@ This preferential etching among amorphous phase and crystalline phase with the different orientation can be explained by the amount of dangling bonds in the silicon films. @FootnoteText@ @footnote 1@ S. Yu, E. Gulari and J. Kanicki, Appl.Phys. Lett., 68, 2681 (1996) @footnote 2@ S. Yu, S. Deshpande, E. Gulari and J. Kanicki, Mat. Res. Soc. Symp. Proc., 377, 69 (1995).

3:20pm **SC+SS+EL-WeA5 Single Ion Impact Effects on Semiconductor and Insulator Surfaces Induced by Slow, Very Highly Charged Ions*, T. Schenkel,*** Lawrence Berkeley National Laboratory*; A.V. Hamza, J.W. McDonald, D.H. Schneider, A. Kraemer, A. Persaud,* Lawrence Livermore National Laboratory

The interaction of slow (<5 keV/u), very highly charged ions, such as Xe@super 44+@ and Au@super 69+@, with solid surfaces is dominated by the deposition of potential energy, rather then the kinetic energy of the ions.@footnote 1,2@ For Au@super 69+@, the sum of the binding energies of the electrons that were removed when forming the ion is 170 keV. This energy is deposited into a nanometer scale area within about 10 fs when an Au@super 69+@ ion impinges on a surface.@footnote 3@ In our presentation we will report on the characterization of undoped silicon after exposure to low doses (~10E11 cm@super -2@) slow, highly charged ions. We recently observed strong photoluminescence at ~565 nm from irradiated silicon surfaces.@footnote 4@ Possible microscopic mechanisms for this effect will be discussed. We will compare atomic force microscopy data from surface defects induced by single ion impacts on mica, self-assembled monolayers and silicon in light of model descriptions of the materials response to the impact of slow, highly charged ions. Acknowledgements: This work is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. Part of this work was performed under the auspices of the U. S. Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48. @FootnoteText@@footnote 1@T. Schenkel et al, Prog. Surf. Sci. 61, 23 (1999) @footnote 2@T. Schenkel, et al., Phys. Rev. Lett. 80, 4325 (1998) @footnote 3@M. Hattass, et al., Phys. Rev. Lett. 82, 4795 (1999) @footnote 4@M. W. Newman, et al., submitted for publication.

3:40pm **SC+SS+EL-WeA6 Ex Situ Removal of Carbon and Oxygen from a Gallium Nitride (0001) Surface*, F. Machuca,*** *Z. Liu, Y Sun, R.F.W. Pease, W.E. Spicer,* Stanford University*; P. Pianetta,* SSRL and Stanford University

We report on a chemical cleaning study of gallium nitride (GaN) using synchrotron radiation to probe the electronic structure of the semiconductor surface and the adsorbed impurities. We study sulfuric peroxide and sulfuric water chemistries for carbon and oxygen removal using the surface sensitive core level information using XPS. We report that a sulfuric peroxide wet treatment followed by a vacuum anneal at 700C reduces C and O concentrations to a few percent of a monolayer. Moreover, this is the first study achieving an atomically clean GaN surface well below the decomposition temperature by 200C. This is a direct result of a weaker form of carbon being chemisorbed to the GaN surface after the peroxide treatment and that is subsequently thermally desorbed. The chemical form is predominantly an oxide of carbon. Whereas the sulfuric water treatment leaves a residual refractive carbon on the surface of GaN in the form of hydrocarbons. These hydrocarbons persist up to the maximum annealing temperature of 740C tested. We also show that by treating the GaN surface with an aggressive oxidizing chemistry like sulfuric peroxide, there is only near monolayer coverages of oxygen. This is direct evidence for the existence of a suboxide on the GaN surface and demonstrates GaN (0001) is not an active surface for bulk oxidation. We also test the effectiveness of the annealing ambient during the thermal desorption portion of the cleaning by comparing vacuum to ammonia annealing. Our findings indicate ammonia is ineffective in aiding thermal desorption of C and O at temperatures at or below 740C, contrary to other reports. Lastly, we offer evidence for a novel oxynitride species on the GaN surface.

4:00pm **SC+SS+EL-WeA7 The Study of InP(100) Chemical Cleaning by Synchrotron Radiation Photoemission Spectroscopy*, Y Sun,*** *F. Machuca, Z. Liu,* Stanford University*; P. Pianetta,* Stanford Synchrotron Radiation Lab*; W.E. Spicer,* Stanford University

The activation process for GaAs negative electron affinity (NEA) photoemitters has been studied extensively. However, the surface chemistry of other NEA materials such as InP is sufficiently different from that of GaAs that additional study is warranted on all aspects of the process starting from the initial surface cleaning to the final activation step. This work will concentrate on the preactivation clean in which the the surface species will be quantified using photoelectron spectroscopy. The goal of this work is to develop clean starting surface that will be used in subsequent activation studies. The cleaning process has three steps, the first two taking place in an argon purged glove bag attached to the load lock of the vacuum system to eliminate atmospheric contamination. Synchrotron radiation is used for the photoemission in order to obtain the necessary surface sensitivity and resolution for the In 4d, P 2p, C 1s and O 1s core levels as well as the valence band. In our most effective cleaning process, the InP is first etched in 4:1:100 H@sub 2@SO@sub 4@:H@sub 2@O@sub 2@:H@sub 2@O and results in a surface with 0.5-1 monolayers of In and P oxides and 0.5-1 ML of C contamination. Note that this is in contrast with GaAs in which this same etching step leaves elemental As and Ga suboxide and thus only requires a subsequent heat treatment to achieve a clean surface. For InP, a second oxide etching step is therefore required. This can either use a 9% HCl or a 1:1 H@sub 2@SO@sub 4@:H@sub 2@O solution both of which result in a hydrophobic surface with 0.3 ML of elemental P, 0.1 ML of C and complete removal of both the P and In oxides,. The lack of any significant amounts of S or Cl on the surface leads us to postulate that this surface is P terminated. Finally, a 360°C anneal in UHV gives a stoichiometric InP surface with no elemental P and only 0.05 ML C. These surfaces are now suitable for similar detailed studies of the full NEA activation process.

4:20pm **SC+SS+EL-WeA8 Ion Irradiation Induced Spontaneous Nanoscale Corrugation on Silicate Glasses*, C.C. Umbach,*** Cornell University*; R.L. Headrick,* Cornell High Energy Synchrotron Source*; K.-C. Chang, J.M. Blakely,* Cornell University

Grazing incidence x-ray scattering was used to determine the temperature and ion-energy dependence of nanoscale corrugations that form on an amorphous SiO@sub 2@ surface eroded by Ar@super +@ ions. The corrugations have wavelengths between 20 and 200 nm with amplitudes of 1 nm. The corrugation wavelength @lambda@@super *@ shows a nearly linear dependence on ion energy for ion energies between 0.5 and 2 keV. Between room temperature and ~300° C, @lambda@@super *@ depends weakly on temperature and above ~300° it shows an Arrhenius-like increase. Ion-assisted viscous relaxation in a thin surface layer is shown to be the dominant smoothing process during erosion;the rate of viscous smoothing scales as (@lambda@@super *@)@super -4@. Similar ion-induced corrugations have also been observed on aluminoborosilicate glasses.

Surface Science
Room 120 - Session SS1-WeA
New Opportunities in Surface Microscopy

Moderator: C.S. Fadley, Lawrence Berkeley National Laboratory

2:00pm **SS1-WeA1 Imaging with Helium Atoms: Developments in Scanning Atom Microscopy***, **D.A. MacLaren**, W. Allison,* University of Cambridge, U.K.

We report on the preparation and production of ultra-smooth helium atom mirrors and on recent advances in the development of a Scanning Atom Microscope (SAM). A bent Si(111)-(1x1)H crystal is an ideal mirror for helium atoms and can be used as the focusing element of a SAM. @footnote 1@ Based upon a focused microprobe of thermal helium atoms, a SAM provides the opportunity for sub-micron, non-destructive and surface-sensitive imaging and could have a profound impact on surface science, particularly in studies of delicate organic systems. A low aberration, high intensity atom mirror requires control over both the macroscopic and microscopic surface properties. Our approach is to bend an ultrasmooth single crystal into the optimum macroscopic profile by application of precise electrostatic fields; we have demonstrated that aberration-free focusing is possible using this method.@footnote 2@ The atom mirror must also have a high helium reflectivity, which requires careful manipulation of the surface microstructure. Here, we discuss refinements to the ex-situ preparation of Si(111)-(1x1)H. Atomic Force Microscopy is used to study the kinetics of the etching mechanism used to produce the mirror surface. We show that small changes in miscut angle can alter the kinetic steady state to promote the formation of deep etch pits and stable self-aligned 'etch hillocks' on the micron scale. Our study has led to the production of surfaces that are homogeneous over tens of microns and which have substantially improved atom reflectivity. The results are a significant improvement in silicon preparation and are a crucial step in the development of a scanning atom microscope. @FootnoteText@ @footnote 1@ B. Holst and W. Allison, Nature (London) 286, (1997), 244. @footnote 2@ D.A. MacLaren, W. Allison and B. Holst, Rev. Sci. Instrum. 71, (2000), 2625.

2:20pm **SS1-WeA2 Scanning Near-Field Infrared Microscopy***, **E.S. Gillman**,* Jefferson Lab

Nanoscale chemical identification of objects below the diffraction limit is possible using a scanned probe technique, the Scanning Near-Field Infrared Microscope (SNFIM). In most cases vibrational spectroscopy in the infrared region is restricted due to the limitations of beam focusing to samples of macroscopic dimensions, on the order of one to several microns. The scale of the measured area is completely determined by the diffraction limit of the incident radiation. With a scanned probe technique resolution of chemical features on the order of @lambda@/20 or ~100 nm can be achieved. An overview of previous experimental results using a free electron laser (FEL)@footnote 1@@super,@@footnote 2@, and more conventional infrared sources@footnote 3@@super,@@footnote 4@, will be discussed. A description of the experiment and recent results from the SNFIM at the Jefferson Lab Free Electron Laser facility will be presented. This work was supported by U.S. DOE Contract No. DE-AC05-84-ER40150, ONR Contract No. N00014-99-1-09B, the Commonwealth of Virginia and the Laser Processing Consortium. @FootnoteText@ @footnote 1@ A. Piednoir, C. Licope, and F. Creuzet, Opt. Commun. 129, 414 (1996). @footnote 2@ M. K. Hong, A. G. Jeung, N. V. Dokholyan, T. I. Smith, H. A. Schwettman, P. Huie and S. Erramilli, Nucl. Instrum. Methods Phys. Res. B 144, 246 (1998). @footnote 3@ B. Knoll and F. Keilmann, Nature 399, 134 (1999). @footnote 4@ C. A. Michaels, S. J. Stranick, L. J. Richter, and R. R. Cavanaugh, J. Appl. Phys. 88, 4832 (2000).

2:40pm **SS1-WeA3 Spectroscopy, Microscopy, and Chemistry at the Spatial Limit***, W. Ho,* University of California, Irvine*; **M. Persson**,* Chalmers University, Sweden **INVITED**

The combination of vibrational spectroscopy and microscopy with the imaging, manipulation, and chemical modification capabilities of the scanning tunneling microscope (STM) has made it possible to probe surface chemistry with sub-Angstrom resolution. Direct visualization of the nature of the chemical bonds and their transformations at the single molecule level not only provides convincing evidences but also fundamental understandings of chemical processes. The STM junction is effectively a nanoreator in which the metallic tip and substrate work together to induce chemical transformations of individual molecules adsorbed either on the substrate or the tip. Many aspects of chemistry can be probed by the STM, including the rotational, vibrational, and translational motions, the conformational changes, the energy transfer, the electrical conductivity, the coupling of electrons to the nuclear motions, and the bond breaking and formation of individual molecules.

3:40pm **SS1-WeA6 Focused Inelasticity in Scanning Tunneling Spectroscopy***, **J.W. Gadzuk**,* National Institute of Standards and Technology*; M. Plihal,* KLA-Tencor

Scanning tunneling microscopy/spectroscopy of magnetic atoms adsorbed upon non-magnetic metal surfaces (possibly Kondo systems) has provided intriguing visual images and spectroscopic signatures in the form of Fano lineshapes in which the asymmetry depends in a diagnostically-useful way on tip location with respect to the adsorbate. Additional STM studies have demonstrated the ability of suitable two-dimensional nanostructures (such as "quantum corrals") to influence the surface electron transport that is part of the total elastic STM process. In a well known paradigm, an elliptical arrangement of Co atoms on Cu(111) gives rise to an apparent enhanced electronic communication between points on the surface which are near the two elliptical foci, showing some behavior consistent with classical ray tracing. The spectroscopic signature of a Kondo atom adsorbed at one focus shows an identical signature (though diminished in intensity) when the STM tip is placed over the vacant focus, suggestive of a mirage or "phantom atom". We report here on similar remote sensing for STM procedures involving inelastic tunneling in which adsorbate-surface or intra-molecular vibrational excitation occurs. We have extended our nonequilibrium theory of scanning tunneling spectroscopy@footnote1@ to include the additional processes, inelastic adsorbate vibrational excitation and elastic surface nanostructure scattering/focusing and the general theory has been applied to an elliptic corral realization. The characteristics of such "focused inelasticity" will be presented within the context of both Kondo systems such as Co/Cu(111) and also simple molecular systems. @FootnoteText@ @footnote 1@ M. Plihal and J. W. Gadzuk, Phys.Rev.B63(2001)085404.

4:00pm **SS1-WeA7 Calculations of Elastic and Vibrational Inelastic Electron Tunneling Images***, **M. Persson**, F. Olsson,* Chalmers University, Sweden*; N. Lorente,* IRSAMC, Univ. P. Sabatier Touluose, France

The inelastic electron tunneling spectroscopy (IETS) in the STM is capable of mapping the vibrational excitation of single molecules in real space with sub-Å spatial resolution and meV spectral resolution.@footnote 1@ Despite the obvious promise of a spectroscopy with these unique capabilities, STM-IETS raises several issues that we need to address by theory to fully exploit this spectroscopy. These issues include; (1) why are so few modes detected; (2) what can be learnt from IET images; (3) what is the nature of the coupling between the tunneling electron and the vibration; (4) what determines the vibrational lineshape ? To this end we have studied the excitation mechanism in STM-IETS using a generalization of Tersoff-Hamann theory to IET combined with density functional calculations.@footnote 2,3@ We have shown that this many-electron theory give quantitative agreement with experiments and have identified several general effects: (1) elastic and inelastic contributions to the IET tend to cancel; (2) a symmetry selection rule connecting the symmetries of the IET images, adsorbate-induced states at the Fermi level and the vibrational mode; (3) a Fano-like lineshape for the second derative of the tunneling current with bias. These effects will be illustrated from a comparison of results of calculated vibrational inelastic images from several systems with experiments, in particular, oxygen adsorbed on silver surface, which provides a typical example of inelastic coupling through a single resonance level.@footnote 4@ We will also illustrate the applicability of the Tersoff-Hamann approximation for the calculations of elastic STM images. @FootnoteText@ @footnote 1@ B.C. Stipe, M.A. Rezaei and W. Ho, Science 208, 1732 (1998); Phys. Rev. Lett. 82, 1724 (1999). @footnote 2@ N. Lorente and M. Persson, Phys. Rev. Lett. 85, 2997 (2000). @footnote 3@ N. Lorente, M. Persson, L. Lauhon, and W. Ho, Phys. Rev. Lett. 86, 2593 (2001). @footnote 4@ J.R. Hahn and W. Ho, Phys. Rev. Lett. 85, 1914 (2000).

4:40pm **SS1-WeA9 Progress in Dynamic Force Microscopy: From High-Resolution Imaging of Insulators to the Measurement of Dissipative Interaction Forces***, **U.D. Schwarz**, H. Hölscher, W. Allers, S. Langkat,* University of Hamburg, Germany*; B. Gotsmann, H. Fuchs,* University of Münster, Germany*; R. Wiesendanger,* University of Hamburg, Germany

Recent progress in dynamic force microscopy (DFM) operated in ultrahigh vacuum, often also called non-contact atomic force microscopy (NC-AFM), enabled the imaging of the atomic structure of surfaces including the observation of point defects independent from the sample's conductivity. However, only few results on insulators have been published so far, possibly due to difficulties in preparing suitable sample surfaces for NC-AFM, e.g., electrostatic charging of the surfaces in vacuum. In order to illustrate the high-resolution capabilities of DFM on insulators, we present the first part of our talk results obtained on NiO(001) at low temperatures. Transition metal oxides are a class of magnetic insulators, which have been of great interest for several decades due to their electronic and magnetic properties. On this material, monatomic defects and atomic resolution across step edges could be observed, achieving a vertical resolution of 1.5 pm. In a second part, the spectroscopic potential of DFM based on a self-driven oscillator set-up is analysed. Introducing a very general tip-sample force law, we show that one of the two quantities measured, the frequency shift, is determined by the mean tip-sample force, while the other quantity, the gain factor (or excitation amplitude), is directly related to dissipative processes like hysteresis or viscous damping. This insight into the measurement principle can be used to examine the contrast mechanism in more detail. The application to non-reactive surfaces like graphite(0001) and xenon(111) allows us to simulate complete DFM images. A comparison between experiment and simulation shows that on xenon, atoms are imaged as maxima, whereas on graphite, the atomic positions of carbon atoms appear as minima and the hollow sites as maxima, in contrast to a simple interpretation of the experimental images.

5:00pm **SS1-WeA10 Characterization of Structure Transition in Ion-Implanted Amorphous Silicon**, ***J.-Y. Cheng***, University of Illinois at Urbana-Champaign; *J.M. Gibson, P.M. Baldo,* Argonne National Laboratory

We use fluctuation electron microscopy to characterize disordered structures in silicon. In fluctuation electron microscopy, variance of dark-field image intensity contains the information of high-order atomic correlations, primarily in medium-range order length scale (1-3nm). In this study, amorphous silicon is produced by self-ion implantation of silicon at liquid nitrogen temprature, followed by annealing processes. As-implanted and annealed structures have been identified as paracrystalline structures and a continuous random network. However, the connection of structure transition to free energy release has not yet been fully understood. We will present new results from materials prepared by post-anneal He irradiation and post-He-bombardment annealing, and discuss effects of He implantation as the system evolves in consecutive treatments.

Surface Science
Room 121 - Session SS2-WeA
Adsorption on Metal Surfaces

Moderator: M.W, Trenary, University of Illinois, Chicago

2:00pm **SS2-WeA1 Chemical Bonding of Alkanes on Metal Surfaces: Adsorption of n-octane on Cu(110)**, ***L. Triguero***, *K. Weiss, H. Öström, D. Nordlund, H. Ogasawara,* Uppsala University, Sweden; *L.G.M. Pettersson,* Stockholm University, Sweden; *A. Nilsson,* Uppsala University; Sweden and Stanford University, Sweden

Using Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy and X-ray emission spectroscopy (XES), we have investigated the electronic structure and chemical bonding of n-octane adsorbed on Cu(110). The high degree of NEXAFS dichroism reveals that the molecule is well oriented on the surface. The NEXAFS spectra also reveal large changes in the unoccupied electronic structure of the adsorbed octane relative to the free molecule. XES, which shows the occupied density of states, reveals new states showing up near the Fermi level. In order to understand these changes in the electronic structure, we have performed cluster model calculations in the framework of Density Functional Theory. The calculations indicate significant charge transfer and formation of a chemical bond between the molecule and the substrate. Our study also gives new experimental evidence of chemical interaction and insights into the bonding mechanism of saturated hydrocarbons adsorbed on metal surfaces, which is of importance for the understanding of the C-H bond activation mechanism.

2:20pm **SS2-WeA2 Two Dimensional Crystallisation of Nucleic Acid Bases on Cu{110}**, ***N.V. Richardson***, *D.J. Frankel, Q. Chen,* University of St Andrews, UK

There is considerable interest in the characterisation and control of biomaterial surfaces. An important step towards this goal is a better, molecular level understanding of model systems based on two dimensional arrays of biorelevant molecules. In this presentation, the adsorption of the nucleic acid bases, uracil (U), thymine (T), cytosine (C), guanine (G) and adenine (A), on Cu{110} has been studied in depth by scanning tunneling microscopy, electron energy loss spectroscopy and low energy electron diffraction. In general, all the molecules form well-ordered 2D structures when vacuum deposited on a room temperature Cu{110} crystal, or at least after moderate annealing. A variety of ordered structures are found for each molecule dependent on coverage and temperature. The pyrimidine bases U, C and T form related structures involving upright molecules and, following loss of hydrogen, adsorbed species in well ordered structures are stable to over 700K. Further heating, results in major re-faceting of the uppermost (ca. ten) layers of the copper substrate giving rise to major new one or two dimensional features. In contrast the purine bases, A and G, form large, two dimensionally ordered domains based on flat-lying molecules without faceting. Hydrogen bonding is a key feature of all the networks. Models of the surface structures will be presented. We also note that although these planar molecules are optically inactive, the single mirror plane is destroyed by adsorption and the resulting surface species is then chiral. This is important in the 2D crystal structures and can result in chiral domains on the surface. .

2:40pm **SS2-WeA3 Electronic State of DNA Molecules on Surface: Cytosine on Cu(110)**, ***M. Furukawa***, Osaka University, Japan; *T. Komeda, M. Kawai,* RIKEN, Japan; *T. Kawai,* Osaka University, Japan; *H. Ogasawara,* RIKEN, Japan; *A. Nilsson,* Uppsala University, Sweden

Electric property of DNA strands and/or molecules being attractive as they are considered to be a candidate for a piece of molecular system in nano-scale technology. The purpose of the present study is to experimentally define the local electronic state of the molecule of the molecular systems by use of x-ray spectroscopies. Here, X-ray photo-electron spectroscopy (XPS) gives the energy level of core sates against the Fermi level, X-ray absorption spectroscopy (XAS) gives the atom specific energy difference between the core state and the state above the Fermi level. Combining all the information then the atom specific view of the energy levels across the Fermi level be understood. Here we give an example for Cytosine adsorbed on Cu(110) surface, where we have observed the core level for C1s, O1s and N1s and XAS from these core levels to the unoccupied states. As for the orientation of the molecule, electric field direction dependence in the XAS experiment for all C, O and N K edge exhibited that the molecular plane of cytosine sits perpendicular to the surface and also parallel to the [1-10] row of the surface. On of the most interesting feature of the electronic states is the fact that the LUMO state of the molecule is found to sit very close to the Fermi level, indicating that the system has a natural tendency to be electron doped conductor is the level is connected in space.

3:00pm **SS2-WeA4 Understanding the Pressure and Structure Gaps in Catalysis: Role of Steps and Terraces in the O@sub 2@ and C@sub 2@H@sub 4@ Interaction with Ag(410)**, *L. Savio, L. Vattuone,* ***M. Rocca***, Universita' di Genova, Italy

The effort to unravel the dynamics of real catalysts by ultra high vacuum investigations of gas-surface interaction suffers of two major limitations, known as pressure gap (10 order of magnitudes difference) and structure gap (the surface of a real catalyst has a high density of steps and defects in contrast to the almost perfect low Miller index surface of a single crystal). A large effort was devoted to bridge the pressure gap; in order to face the structure gap, attention was focused on defected surfaces, obtained either by ion bombardment or by cutting a single crystal along vicinal planes. We report on a combined supersonic molecular beam and High Resolution Electron Energy Loss Spectroscopy investigation of the angle and energy dependence of the sticking probability, S, of O2 and C2H4 on Ag(410), a vicinal surface with (100) teraces and (110) step edges. In agreement with our previous results for the ion bombarded Ag(100) surface, we find for O2 adsorption that dissociation and molecular chemisorption coexist already at temperatures at which only molecular adsorption is stable on flat Ag(100). The angular dependence of S shows that when the molecules impinge against the step edges the activation barrier for molecular adsorption is strongly reduced or even eliminated. The reactivity of Ag atoms at terrace sites is, on the contrary, reduced with respect to the flat surface. Dissociation takes place preferentially at the upper side of the steps as proven by the temperature and angular dependence of S. For C2H4 we observe nearly unitary sticking probability at the step edge and stable adsorption in the pi-bonded state. S scales approximatively with total energy, but it is slightly larger for molecules impinging grazing on the step edges and decreases when the step edges are in shadow. The interaction is mediated by an extrinsic precursor.

3:20pm **SS2-WeA5 Chemical Bonding in Structurally Complex Chemisorption Systems*, D.A. King,*** University of Cambridge, UK, U.K. **INVITED**

The combination of (i) quantitative LEED, infrared and STM structural analyses of complex adsorbate structures with (ii) SCAC (single crystal adsorption calorimetry) measurements of energetics, on the one hand, and state-of-the-art first principles DFT slab calculations of these systems on the other has provided a unique experimentally benchmarked approach to chemical bonding in structurally complex chemisorption systems.@footnote 1@ Of particular importance to reactivity in molecular systems at surfaces, this has given rise to the new concept of surface and promoter-induced molecular polarisation, and its relationship to stereo-electronically driven chemical reactivity in catalysis.@footnote 2@ The presentation will draw particularly on our recent results for CO + K coadsorption on Co{1010},@footnote 2-4@ C@sub 6@H@sub 6@ adsorption on Ni{111}@footnote 5@ and on Ir{100}@footnote 6@ and coadsorption with O, CO and NO on Ni{111}@footnote 7@ and anisole adsorption on Pt{110}.@footnote 8@ @FootnoteText@ @footnote 1@"Adsorption Energetics and Bonding from Femtomole Calorimetry and from First Principles Theory", Advances in Catalysis, 43 (2000) 207-259. @footnote 2@Q. Ge, R. Kose and D. A. King. "A Role for Induced Molecular Polarisation in Catalytic Promotion: CO Coadsorbed with K on Co{1010}", J. Am. Chem. Soc., 122 (2000) 10610-10614. @footnote 3@S. J. Jenkins and D. A. King. "Full Structure Determination of an Alkali Metal/CO Co-Adsorption Phase, for Co{1010} (2x2)-(K + CO)", Phys. Rev. B, 51 (1995) 17063-17067. @footnote 4@P. Kaukasoina, M. Lindroos, P. Hu, D. A. King and C. J. Barnes. "The Coadsorption of CO and K on Co{1010}", Surf. Sci., 349 (1996) 19-42. @footnote 5@R. L. Toomes and D. A. King "Realistic Molecular Distortions and Strong Substrate Buckling Induced by the Chemisorption of Benzene on Ni{111}", J. Chem. Phys, 105 (1996) 11305-11312. @footnote 6@G. Held, M. P. Bessent, S. Titmuss and D. A. King. "Benzene Adsorption on Ir{100} Studied by LEED I-V Analysis: Evidence for Formation of Tilted Benzyne", J. Chem. Phys., in press. @footnote 7@K. Johnson, B. Sauerhammer, S. Titmuss and D. A. King. S. Titmuss, D. A. King, to be published. @footnote 8@Y. P. Tan, S. Khatua, S. Jenkins and D. A. King, to be published.

4:00pm **SS2-WeA7 The Dynamics of CO and H co-adsorption on Ru(0001)***, B. Riedmüller,* FOM Institute for Atomic and Molecular Physics, The Netherlands*; I.M. Ciobica, R.A. van Santen,* Eindhoven University of Technology, The Netherlands*; **A.W. Kleyn,*** Leiden University, The Netherlands

Chemical reactions at surfaces form an exciting example of co-adsorbate systems on surfaces. The dynamics of such systems is still poorly understood. In this paper we will consider the dynamics of CO and H co-adsorption on Ru(0001). In earlier experiments we have demonstrated that H-adsorption turns the Ru surface in an almost perfect inert mirror for CO molecules. However, the sticking probability does not go to zero. There are adsorbing spots on the mirror. We carried out DFT calculations that demonstrate the nature of the activated adsorption of CO on H-Ru(0001). There is one specific site (atop) exclusively binding CO. In contrast, at the clean surface the entire unit cell strongly binds CO, and the molecule will reside at the most strongly bound site. This means that the reactivity of the H-covered surface strongly varies over distances of much less than an Angstrom. The nature of the bonding will be elucidated. Although we have computed a stable CO-H-Ru(0001) configuration this does not mean that this is the most stable. In fact the system shows phase separation. We studied its formation by Thermal Energy Atom Scattering. We find that on adsorption of CO on a H-Ru(0001) surface the CO nucleates in islands. The island size depends on the CO flux. In contrast to what has been seen for epitaxy of metals on metals at low CO flux small 'magic' CO-7 clusters are formed, at high flux large islands nucleate.

4:20pm **SS2-WeA8 Ordered Structures of CO on Pd(111) Studied by STM*, M.K. Rose,*** Lawrence Berkeley National Laboratory and University of California at Berkeley*; J.C. Dunphy, T. Mitsui,* Lawrence Berkeley National Laboratory*; A. Borg,* Norwegian University of Science and Technology, Norway*; D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory

The @sr@3x@sr@3-R30°, c(4x2), and (2x2)-3CO structures of CO on Pd(111) have been studied by STM. Shifts of the CO binding site with increasing coverage are observed. At coverages of 1/3 ML and below, CO occupies three-fold hollow sites. Near 1/2 ML, regions of c(4x2) CO with both FCC and HCP three-fold hollow site occupation coexist with bridge bonded c(4x2) CO. At high coverage, a partially disordered phase with no top site occupation directly precedes formation of the 2x2 structure. With additional adsorption of CO, bright maxima appear with 2x2 periodicity. The maxima at the edge of 2x2 domains exhibit a quasi-continuous range of corrugation, implying a gradual shift of CO to top sites. The high corrugation of top site CO obscures the other two CO molecules per unit cell, resulting in a symmetric 2x2 periodicity. In addition to this symmetric 2x2 structure, previously unreported domains of lower symmetry 2x2 are observed.

4:40pm **SS2-WeA9 Bridging the Pressure Gap at the Atomic Level*, P. Thostrup,*** *L Österlund, I. Stensgaard, E. Laegsgaard, F. Besenbacher,* University of Aarhus, Denmark

Surface science studies conducted under ultrahigh vacuum (UHV) conditions have contributed immensely to our current knowledge about catalytic processes. A fundamental question is however still, whether UHV data are in general applicable at technologically relevant pressures magnitudes higher than those obtainable in UHV studies. We have developed a novel high-pressure scanning tunneling microscope (HP-STM)@footnote 1@ in order to compare eg. the UHV and HP response of the H/Cu(110) and CO/Pt(110) systems. The H/Cu(110) system is a classic model system for activated dissociation. We find that hydrogen reconstructs the surface both at UHV and high pressures. Through a detailed comparison we even find quantitative agreement between HP and UHV data,@footnote 2@ thus providing support for the surface science approach to heterogeneous catalysis. The CO/Pt(110) system has attracted widespread attention since CO displays an unusually strong dependence upon the coordination number of the Pt atom to which it binds. This property makes the open Pt(110) surface ideal for HP experiments since high pressures of CO are expected to induce massive roughening of the surface. Notwithstanding, already in UHV this interesting property reveals itself:@footnote 3@ We find the equilibrium structure at intermediate coverages to be extremely rough to an extent where almost all top-layer Pt atoms are at steps. Interestingly, we have been able to reproduce this behavior quantitatively in Monte Carlo simulations where all energies involved are taken from ab initio density functional calculations. Preliminary experiments indicate that the roughening behavior described above is also present at high pressures, but in this case to an even more extensive degree. @FootnoteText@ @footnote 1@ E. Laegsgaard, P. Thostup et al., submitted to Rev. Sci. Instr. @footnote 2@ L. Österlund, P. Thostrup et al., Phys. Rev. Lett. 86, 460 (2001). @footnote 3@ P. Thostrup et al., submitted to Phys. Rev. Lett.

5:00pm **SS2-WeA10 A Single-crystal Adsorption Calorimeter for Low Vapor Pressure Molecules*, H. Ihm,*** *H.M. Ajo, C.T. Campbell,* University of Washington

We report a new microcalorimeter for measuring heats of adsorption of low vapor pressure molecules on clean single crystals. While temperature programmed desorption (TPD) and isosteric measurements can provide information on heats of adsorption, they are limited to reversible adsorption-desorption processes. In many catalytically interesting cases, adsorbates undergo irreversible chemical changes upon adsorption or heating. Our microcalorimeter enables direct measurement of these adsorption energies. The principle is similar to that pioneered by King's group:@footnote 1@ a pulse of gas from a molecular beam impinges on a 1 µm-thick single crystal surface. The incident molecules adsorb either physically or chemically, causing a transient temperature rise. This heat input is detected by a 9 µm thick pyroelectric polymer ribbon, which is mechanically driven to make gentle contact with the back of the single crystal sample during a calorimetry measurement.@footnote 2@ This process allows the determination of heats of adsorption as a function of coverage with femtomole resolution. While King's group has performed beautiful adsorption calorimetry, their measurements have been limited to high vapor pressure gases. We have added a specially designed molecular beam source for low vapor pressure molecules, thus significantly extending the capabilities of this technique. Sticking probabilities and absolute coverages are measured by quadrupole mass spectrometry (QMS), low energy ion scattering (LEIS), x-ray photoelectron spectroscopy (XPS), and TPD. As a first experiment, we present a microcalorimetric measurement of benzene adsorption on Pt(111). @FootnoteText@ @footnote 1@ W.A. Brown, R. Kose, and D.A. King, Chem. Rev. 98, 797 (1998). @footnote 2@ J.T. Stuckless, N.A. Frei, and C.T. Campbell, Rev. Sci. Instruments, 69, 2427 (1998).

Surface Science
Room 122 - Session SS3-WeA

Electronic Structure I

Moderator: S.D. Kevan, University of Oregon

2:00pm **SS3-WeA1 Medard W. Welch Award Lecture: Intertwined Charge Density Wave and Defect-Ordering Phase Transitions in a 2-D System@footnote 1@***, **E.W. Plummer,*** The University of Tennessee and Oak Ridge National Laboratory, US*; A.V. Melechko,* The University of Tennessee and Oak Ridge National Laboratory **INVITED**

The study of macroscopic properties of phase transitions in low-dimensional systems provides an understanding of the fundamental aspects of systems of interacting particles. Phase transitions are strongly affected by defects, especially in systems with lower dimensionality. In quasi-1D or -2D systems that exhibit a CDW transition, a small proportion of microscopic disorder can control the global properties because of the collective nature of the phenomena. It has been speculated that the interaction of mobile defects with CDW leads to alignment of defects with the CDW, or the formation of Defect Density Waves.@footnote 2@ In this dynamic picture, the distribution of defects is neither random nor static, instead defects align their positions to optimize the energy of the pinned CDW. Here, we will discuss a complex symmetry lowering (Ã3xÃ3) to (3x3) phase transition in Sn/Ge(111) and similar systems that can be decomposed into two intertwined phase transitions: a second order CDW transition and a first order disorder-order transition in the defect distribution. We present two phenomenological models that describe these transitions and their interrelation.@footnote 3@ These models allow us to understand the formation of the domains and domain walls seen in STM at low temperatures, defect-induced waves above the CDW transition temperature, and ordering of the defects caused by the CDW-mediated defect-defect interactions.@footnote 4@ The models predict a shift in the CDW transition temperature with impurity density and a dependence of the (3x3) lattice structure on the specific defect alignment. @FootnoteText@ @footnote 1@ Supported by NSF DMR 980130. ORNL is supported by the U.S. DOE through contract DE-AC)5-))OR22725 with UT-Battelle, LLCC.@footnote 2@ H. Mutka, in Advances in the crystallographic and microstructural analysis of charge density wave modulated crystals, edited by F. W. Boswell and J. C. Bennet, Kluwer Academic Publishers, Dordrecht, 1999.@footnote 3@ A. V. Melechko, M. Simkin, N. F. Samatova, J. Braun, and E. W. Plummer, submitted for publication.@footnote 4@ A. V. Melechko, J. Braun, H. H. Weitering, and E. W. Plummer, Phys. Rev. Letters, 83, 999 (1999). H. H. Weitering, A. Melesko, J. M. Carpinelli, and E. W. Plummer, Science, 285, 2107-2110 (1999).

2:40pm **SS3-WeA3 Lifetimes of Surface States at Si(001) Surfaces*, M. Weinelt,*** *M. Kutschera, C. Kentsch, Ch. Orth, Th. Fauster,* Universität Erlangen-Nürnberg, Germany

With ultrafast two-photon photoemission spectroscopy the temporal evolution of an excited electronic system can be studied on the femtosecond time scale. A pump pulse excites electrons to distinct intermediate states while a second time-delayed pulse probes the evolving population dynamics. This allows to determine lifetimes of conduction bands and unoccupied dangling-bond states on semiconductor surfaces directly in the time domain. Using time-resolved two-photon photoemission we have studied the c(4 x 2) and (2 x 1) reconstructions of the Si(100) surface. Several bulk and surface transitions involving unoccupied intermediate states below the vacuum energy are identified. In particular, the surface band gap at the center of the surface Brillouin zone, i.e., the gap between occupied and unoccupied dangling-bond states is determined to 0.96 ± 0.05 eV. The unoccupied dangling-bond state shows a rich dynamic ranging from fs to more than 100 ps. Population and decay are dominated by electron-phonon scattering which couples bulk and surface states. The decay rate is strongly influenced by surface defects in the band gap.

3:20pm **SS3-WeA5 Electronic Structure of Complex Manganite Spinels Studied by XPS, XANES, EXAFS and Nanoprobe EELS*, D.A. KuKuruznyak,*** *B.W. Reed, J.G. Moyer, M.C. Gregg, S.-W. Han, E.A. Stern, M. Sarikaya, F.S. Ohuchi,* University of Washington

Ni-Co-Cu-Mn-O spinels, owing to their strong temperature influence on resistivity, are technologically important oxide materials for thermistor applications, among which Ni@sub 0.48@Co@sub 0.24@Cu@sub x@Mn@sub 2.28-x@O@sub 4@ (x = 0.6, and 1.2) are the compositions of specific industrial interests. In this study, we synthesized nanocrystalline thin films and powders using low temperature metallorganic decomposition technique, rather than conventional solid state sintering. The materials were subsequently annealed at temperatures between 500 and 800°C, and it was found that annealing temperature was a decisive factor in controlling transport properties. Electronic structure of the bulk and surface was investigated by combinations of XPS, XANES, and nanoprobe EELS. The analysis revealed that the annealing caused change of the oxidation state from Cu@super 1+@ to Cu@super 2+@, which was accompanied by reduction of manganese cations from Mn@super 4+@ to Mn@super 3+@. EXAFS analysis showed that both the Cu@super 1+@ and Cu@super 2+@ ions occupied the tetrahedral lattice sites, whereas both the Mn@super 4+@ and Mn@super 3+@ were in the octahedral sites in the spinel structure. During the course of annealing, an unusually large negative binding energy shift in both Cu 2p and Cu 3d levels for the Cu@super 1+@ state was observed. This negative shift appears to be unique to this system, and was attributed to the change in the Fermi surface topology due to strong 3d-4p hybridization which occurs in the in the tetrahedral coordination because of the completely filled 3d@super 10@ orbital of Cu@super 1+@ ion.

3:40pm **SS3-WeA6 Quantum Well Behavior without Confining Barrier Observed via the Dynamically Screened Photon Field***, S.R. Barman,* Inter-University Consortium for DAE Facilities*; **P. Haberle,*** Universidad Tecnica Federico Santa Maria*; K. Horn,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany*; J. Maytorena,* Universidad Nacional Autonoma de Mexico*; A. Liebsch,* Forschungszentrum Julich, Germany

Quantum well states are a striking manifestation of elementary quantum mechanics. An electron confined in a one-dimensional potential well, formed by the vacuum on one side and a band gap in the substrate on the other, may occupy discrete energy levels whose quantum number specifies the number of half-wavelengths spanning the well. Angle resolved photoemission spectra from Na adlayers on Al(111) reveal features which behave as quantum well resonances, even though the substrate does not provide a barrier for electron confinement. These features are observed in a narrow photon energy range where overlayer collective excitations cause resonant enhancement of the photoemission intensity. The quantum well behavior is shown to be due to surface resonances of the Na/Al system. These are observable since the screened photon field is dynamically enhanced and spatially confined to the overlayer. The special role of the photon field distinguishes the present system from ordinary quantum wells. The quantum well-like spectral features are associated with virtual states induced by the large negative potential step between overlayer and substrate. To observe these resonances it is crucial to suppress emission from substrate bands in the same energy region. This is achieved by tuning the photon energy to the collective modes of the overlayer. The local electric field is then enhanced and confined to the overlayer so that the Na resonances can be observed in a wide range of coverages. Thus, while in usual quantum well systems the photon field plays no special role, here it serves as a novel mechanism ensuring the confinement of the excitation region.

4:00pm **SS3-WeA7 Molecular Resonant Quantum Wells at Organic-Metal Interfaces*, G. Dutton,*** *X.-Y. Zhu,* University of Minnesota

Quantum-well like molecular resonances have been observed in electron transfer at a model molecule/metal interface: C6F6/Cu(111). Two photoemission measurement reveals a transient molecular anionic resonance located at 3 eV above the Fermi level. This mol ecular resonance is dispersed parallel to the surface, i.e. resonant quantum well behavior. Both the energetic position and the dispersion of this molecular resonance depend intimately on the interfacial electronic structure and the strength of molecule-s urface interaction. With increasing coverage of pre-adsorbed atomic hydrogen which weakens molecule-surface interaction, the position of molecular resonance in C6F6 increases while the effective electron mass decreases. We conclude that the resonant molecular quantum well is confined to the interface and is a result of both molecule-molecule and molecule-surface interaction.

4:20pm **SS3-WeA8 Dynamics of Photo Excited Carrier Trapping and Recombination at Si(111) Interfaces Probed By Time-Resolved Second Harmonic Generation*, D. Bodlaki,*** *E. Borguet,* University of Pittsburgh

Carrier trapping and recombination is the primary fate of conduction band electrons. Interfaces are known to play an important role in these processes. However, probing the interface is challenging as the interface represents but a small fraction of the total number of atoms in a macroscopic sample. Distinguishing between photoprocesses due to surface states and those from excitation of states in the bulk, resulting from crystal impurities or defects, is difficult especially if one is monitoring a bulk property such as photocurrent. Second Harmonic Generation (SHG) is known to be a versatile in-situ, real time probe of buried interfaces. In this study SHG was used to probe carrier relaxation at various Si interfaces and to asses the passivating nature of the surface. Carriers were created by optical excitation via an interband transition induced by an 800 nm, 4 psec pump pulse. Subsequently, the nonlinear optical response of the interface was probed by SHG of 800 nm light. The SHG dynamics depend strongly on the surface chemistry. Native oxide covered surfaces exhibit an initial increase in SHG response followed by a linear decay on a nanosecond timescale. Surface modification changes the dynamics. RCA cleaned, oxide covered samples also show an initial increase in SHG response, but the subsequent decay appears slower. H terminated surfaces show distinctively different behavior: initially the SHG signal decreases then recovers faster then the oxide covered silicon. The different dynamics probably reflect the degree of interface passivation. Defect sites deplete the conduction band carrier population by trapping or recombination.

4:40pm **SS3-WeA9 Surface Femtochemistry: Observing and Controling Adsorbate Motion on Metal Surfaces on Femtosecond Time Scale*, H. Petek,*** University of Pittsburgh **INVITED**

Electronic and nuclear dynamics of alkali atoms adsorbed on noble metal surfaces are investigated in real time by the interferometric time-resolved two-photon photoemission technique.@footnote 1@ Photoinduced charge transfer with a <20 fs laser pulse turns on repulsive Coulomb force between alkali atoms and the substrate, thereby initiating desorption from the surface. The resulting nuclear wave packet motion is detected through changes in the surface electronic structure. In the extreme case of Cs/Cu(111), the alkali atom desorptive motion can be observed for up to 200 fs, which according to a Newton's law model corresponds to stretching of the Cu-Cs bond by ~0.3 Å.@footnote 2@ Furthermore, the coherent polarization created by the charge-transfer excitation persists for up to 60 fs. Demonstration of quantum control, whereby it is possible to generate displaced ground and excited state wave packets, is accomplished by interference between the pump and probe excited polarization in the sample.@footnote 3@ However, the photodesorption process is frustrated by the wave packet spreading and decay through recoil-induced phonon generation, reverse charge transfer, and electron inelastic scattering, which induce the phase and energy relaxation.@footnote 4@ Prospects of controlling the electronic and nuclear motion of atoms and molecules at surfaces will be discussed. @FootnoteText@ @footnote 1@S. Ogawa, H. Nagano, and H. Petek, Phys. Rev. Lett. 82, 1931 (1999). @footnote 2@H. Petek, H. Nagano, M. J. Weida, and S. Ogawa, Science 288, 1402 (2000). @footnote 3@H. Petek, M. J. Weida, H. Nagano, and S. Ogawa, J. Phys. Chem. A 104, 10234 (2000). @footnote 4@H. Petek, H. Nagano, M. J. Weida, and S. Ogawa, J. Phys. Chem. (Feature Article; in press). .

Thin Films
Room 123 - Session TF-WeA
Nucleation and Growth

Moderator: H. Jeon, Hanyang University, Korea

2:00pm **TF-WeA1 Spectroscopic Ellipsometry Studies on Film Smoothness of Sputtered Thin Films@footnote 1@*, C. Liu,*** *J. Erdmann, A. Macrander,* Argonne National Laboratory

For x-ray mirrors, it is very important to have the surface roughness controlled at less than a few @Ao@ rms. Sophisticated polishing techniques have been developed to obtain substrate roughness less than 3 @Ao@. Quite often, x-ray mirrors are coated with various metals for optimum reflectivity at selected energies. One needs to make sure that the coating process will not introduce excess roughness. Spectroscopic ellipsometry has been broadly used for film thickness and morphology measurements. Here we report a new method to study the smoothness for films that are usually too thick for an ellipsometer to measure. We found that a thin C film usually follows the substrate morphology and will not introduce additional roughness. A thin C film was grown on the film to be studied; ellipsometry measurements were then carried out. The ellipsometry data were fit with both a flat-film and rough-film model to obtain the film smoothness information. Results of C/Au, C/W, and C/Cu films on Si and glass substrates will be discussed. @FootnoteText@ @footnote 1@This work is supported by the U. S. Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-ENG-38.

3:20pm **TF-WeA5 Quantum Size Effects in 2D Pb Islands on Si(111)*, C.S. Chang,*** *W.B. Su,* Academia Sinica, Taiwan, ROC*; S.H. Chang,* National Tsing Hua University, Taiwan, ROC*; W.B. Jian,* Academia Sinica, Taiwan, ROC*; L.J. Chen,* National Tsing Hua University, Taiwan, ROC, Taiwan, R.O.C.*; T.T. Tsong,* Academia Sinica, Taiwan, ROC

When the thickness of a metallic film approaches a few atomic layers, the de Broglie wavelength of its Fermi electrons becomes comparable to film thickness and quantum size effects (QSE) begin to appear. These effects, though originated from the electron confinement, can have a profound effect on various nano scale physical properties. For instance, Schulte@footnote 1@ earlier calculated the film thickness dependence of electron densities, potentials and work functions for free standing metal films and found oscillations in all these quantities. In addition, when the effect of discrete lattice is taken into account, the QSE can invoke the structural variations also. All these findings exemplify the unusual behavior of thin metal films varying with their thickness. However, clear experimental evidence directly relating quantized electronic states to interlayer relaxations of individual islands is still lacking. The first observation of the QSE for individual Pb islands grown on the Si(111) surface has been made by Altfeder et al.,@footnote 2@ and we have extended their work toward thinner films. Also in this study, individual 2D lead (Pb) islands of varying heights grown on the Si(111)7x7 surface at low temperature are investigated concurrently with real-space and local-probe scanning tunneling microscopy and spectroscopy. Quantum size effects, manifested as quantized electronic states and oscillatory relaxations in interlayer spacings are found perfectly correlated to each other. @FootnoteText@@footnote 1@F. K. Schulte, Surf. Sci. 55, 427 (1976). @footnote 2@I.B. Altfeder, K.A. Matveev, and D.M. Chen, Phys. Rev. Lett. 78, 2815 (1997).

3:40pm **TF-WeA6 In situ and Ex Situ Surface Dangling Bond Measurements on a-Si:H by Means of Surface Cavity Ring Down Absorption***, A.H.M. Smets, J.H. van Helden,* ***M.C.M. van de Sanden,*** Eindhoven University of Technology, The Netherlands

The study of surface dangling bonds during growth of hydrogenated amorphous silicon (a-Si:H) is of great importance because of their possible role as dominant growth sites. In this contribution we will introduce a new technique, surface cavity ring down absorption (SCRDA), which enables us to measure directly small absorptions (10@super -5@ - 10@super -2@) by surface dangling bonds. The sensitive SCRDA technique is based up on the rate of absorption of a light pulse confined between two highly reflective mirrors in an optical cavity configuration. Ex situ single wavelength measurements (@lambda@ = 1064 nm, @tau@@pulse@ = 10 ns, E@pulse in cavity@ = ± 1 µJ) on a-Si:H films (10-3000 nm) on Corning glass show that the SCRDA technique is able to detect the surface dangling bonds. The obtained surface defect density of the a-Si:H oxidized surface is around 10@super 12@ cm@super -2@ and is in agreement with electron spin resonance (ESR) and photothermal deflection spectroscopy (PDS) results. Furthermore, it is demonstrated that the surface roughness, as determined from AFM measurements, correlates with the surface defect density. In situ SCRDA measurements are performed using a mirror - prism (suprasil) - mirror cavity configuration in which the light pulse incidents perpendicular on the two 70° tilted prism surfaces and has a total internal reflection on the backside surface. The initial a-Si:H growth phase (approx. 20 nm) has been monitored. The surface defect density increases up to the not yet saturated value of about 10@super 13@ cm@super -2@ in agreement with reported results using in situ ESR measurements. This value is higher than expected from reported growth models (10@super 9@ - 10@super 12@ cm@super -2@) in which the defect density is determined by the creation and passivation of surface defects by weakly absorbed radicals. The implications for the growth mechanism of a-Si:H will be discussed.

4:00pm **TF-WeA7 Nanostructured Responsive Surfaces*, J. Liu,*** Lucent Bell Laboratories **INVITED**

This presentation discusses the design and synthesis of nanostructured materials and films with multifunctional responsive surfaces. The electronic, optical, and dielectric properties of various nanostructured films have been widely investigated. More recently, there has been a growing interest in these materials for health and biomedical applications. Two key areas of research have been pursued: (1) the formation of the nanostructures themselves on a multilength scale, and (2) the incorporation of the recognition and responsive properties. On a molecular level, techniques such as molecular imprinting have been explored. On the nano- and sub micrometer length scale, self-assembly and super-molecular templating have attracted wide attention. On the micro- and macrolength scale, micro machining and lithography have been extensively used. In addition, novel synthesis methods have been developed to incorporate active sites and functionalities so that the nanostructured hosts can selectively recognize, or even respond to the change of the environment. For molecular recognition, selective ligands, or size-and-shape selective cage structures, are introduced. For responsive properties, environmental sensitive polymers, or other switchable organic molecules, are investigated. The challenge is to integrate the nanostructured materials and the functionalities on different length scales so that the whole material will have the proper chemical and physical properties, and will detect and respond to the change in the environment. Many examples from our own research, as well as from other groups, will be given to illustrate the potential of the integrated approaches.

4:40pm **TF-WeA9 Connecting the Evolution and Coalescence of 3-dimensional Grain Structures to Reactor-scale Phenomena***, **M.O. Bloomfield**, D.F. Richards, O. Klaas, J. Lu, A.M. Maniatty, M.S. Shepard, T.S. Cale,* Rensselaer Polytechnic Institute

We have created a finite-element based, multiple level-set code to model the evolution and coalescence of grains and atomic scale islands during thin film growth. Our software tool can simulate the evolution of N grains or atomic-scale proto-grains. Grain boundaries are represented implicitly by a set of N+1 scalar fields, phi@sub i@(r,t) expressed on an unstructured mesh, subject to the condition that phi@sub i@(r,t) = 0 for all r on the boundary of grain i at time t.@footnote 1@ By extracting the zero contour, we can recover the grain boundaries at any time. Because each grain is associated with its own scalar field, properties such as lattice orientation can be easily retained on a grain-by-grain basis. The evolution of each grain is computed separately using the usual level set equation. We use an explicit positive coefficient scheme for this evolution. Level sets representing different regions are then reconciled to bring the them into agreement. To address distortions in the scalar fields, we implement a "redistancing" algorithm that corrects these distortions. This step stabilizes the evolution, allowing for simulations that include the coalescense of proto-grains and islands into complex grain structures. Demonstrations of this code are presented, including applications within a multiscale framework. Reactor scale simulations of reactant transport are performed using an FEM code. Reactant data are passed to this scale from the grain scale in the form of boundary conditions. This allows us to establish concentration fields of reactant both on the scale of 0.1 m, and using local refinement, on the 0.1 mm scale. The reactor-scale simulation passes reactant data back down to a grain-scale level set simulation. This allows us to show the interaction of phenomena such as reactor-scale reactant depletion on the resulting grain structure. @FootnoteText@ @footnote 1@Osher, S. and Sethian, J.A., J. Comput. Phys. 79, 12 (1988).

5:00pm **TF-WeA10 Sputter Deposition of Metallic Sponges***, **A.F. Jankowski**,* Lawrence Livermore National Laboratory

The growth of thin-film metallic sponges is of interest in several electrochemical applications, for example, conductive porous electrodes for gas transport and processing.@footnote 1@ Determination of the experimental parameters needed to yield metallic sponges should be tractable for physical vapor deposition processes. The general guidelines on how to stabilize the basic coating morphologies are found in the classic zone model for film growth.@footnote 2@ It's known that morphologies in structure can range from porous columnar to dense polycrystalline as the process conditions are manipulated for either sputter deposition or evaporation. However, there's no reference to the three-dimensional structure of a sponge - that is, a polycrystal with continuous open porosity but without the definitive columnar features characteristic of vapor deposits. Herein, conditions for deposition are resolved that produce the sponge morphology augmenting the classic zone model of structure. For sputter deposition using planar magnetrons, the general conditions are an increased working gas pressure and an intermediate substrate temperature. Example results of the sponge morphology in a 1 to 2 µm thick coating are presented for metals including aluminum, gold, nickel, and silver. This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48. @FootnoteText@ @footnote 1@ A. Jankowski, et al., J. Vac. Sci. Technol. A, 13 (1995) 658; 18 (2000) 2003. @footnote 2@ J. Thornton, J. Vac. Sci. Technol., 14 (1974) 666.

Tribology
Room 132 - Session TR+MM-WeA
Nanotribology

Moderator: Y.-W. Chung, Northwestern University

2:00pm **TR+MM-WeA1 Tribological Issues in MEMS***, **R. Maboudian**,* University of California, Berkeley **INVITED**

Given the dimension of most microelectromechanical systems, gravity and other body forces are negligible. In contrast, interfacial forces dominate due to their large surface area-to-volume ratios. As a consequence, adhesion, friction, and wear are prevalent problems in many MEMS devices. Additionally, MEMS technology provides us with the opportunity to study tribology on a length scale not easily accessible by other techniques, namely the mesoscopic length scale. This presentation will discuss the use of several tribological microinstruments in conjunction with other surface characterization techniques, such as atomic force microscopy, to measure the surface forces present between polycrystalline silicon surfaces and to manipulate them by utilizing various surface treatments. The successes and the limitations of current surface coating technologies as well as areas for improvement will be discussed.

2:40pm **TR+MM-WeA3 Friction Properties of Self-assembled Monolayers: Influence of Adsorbate Molecular Structure and Molecular Organisation***, N.J. Brewer, **G.J. Leggett**,* UMIST, UK **INVITED**

The frictional properties of self-assembled monolayers (SAMs) of alkanethiols on gold are influenced by both the chemistry of the adsorbate tail groups and the organisation of adsorbate molecules within the monolayer. Studies of mixed self-assembled monolayers composed of adsorbates with contrasting terminal group chemistries and equal chain lengths have revealed a linear relationship between SAM composition and the coefficient of friction. However, for mixed SAMs formed from molecules with differing alkyl chain lengths, molecular organisation may be quite different from that observed for single component SAMs, leading to substantial changes in the coefficient of friction. Moreover, while methyl terminated SAMs exhibit markedly different frictional properties for adsorbates of different chain length, this is not the case for SAMs formed from hydroxyl and carboxylic acid terminated adsorbates. For these polar SAMs the coefficient of friction varies little between short and long chain adsorbates. This is attributed to hydrogen bonding between adsorbate terminal groups, which has a dominating effect on SAM stability and organisation. The friction-velocity behaviour of SAMs with polar terminal groups in contact with polar tips is quite different from the behaviour observed for the same materials in contact with non-polar tips, and the expected linear relationship between the friction force and the log of the velocity is not observed; instead the friction force rises rapidly and then reaches a plateau. Finally, friction properties of specific thiols adsorbed onto gold and silver surfaces are markedly different, reflecting changes in molecular organisation and providing valuable insights into the structures of these materials.

3:20pm **TR+MM-WeA5 Interfacial Friction of Methanol Sliding on Rigid vs. Rotating Fullerenes***, **T.S. Coffey**, M. Abdelmaksoud, J. Krim,* North Carolina State University

Due to the ability of C60 molecules to rapidly rotate within their lattice position, tribologists had hopes that C60 molecules would work like nano-sized ball bearings. C60 has not been proven to be an effective lubricant. We measured the interfacial friction of toluene on Ag(111) in both the presence and absence of interfacial C60 layers employing quartz crystal microbalance (QCM) and atomic force microscopy (AFM) techniques.@footnote 1@ We see the friction double when C60 is present. However, the difference in interfacial friction between a rigid vs. a rotating molecule in a substrate remains an interesting topic. C60 is known to form close packed hexagonal films on both Ag(111) and Cu(111) substrates. However, on Ag(111) surfaces, C60 is known to spin freely in its lattice position, while it is not free to rotate on a Cu(111) surface.@footnote 2@ In order to determine whether the spinning of the C60 molecules affects the interfacial friction, we are employing QCM techniques to compare the friction of methanol on C60/Ag(111) vs. methanol on C60/Cu(111). We examine here whether the rolling nature of the C60 layer impacts the sliding friction as probed by QCM, AFM, and QCM/STM measurements. @FootnoteText@ @footnote 1@ T. Coffey, M. Abdelmaksoud, and J. Krim, "A Scanning Probe and Quartz Crystal Microbalance Study of the Impact of C60 on Friction at Solid-Liquid Interfaces", Journal of Physics Condensed Matter, in press. @footnote 2@ Applied Surface Science 87/88 (1995) 405.

4:00pm **TR+MM-WeA7 Superconductivity Dependent Friction of Adsorbed Monolayers on Pb(111)**, ***J. Krim***, *A. Mayer, L. Wagner,* North Carolina State University

In order to gain a fundamental understanding of friction, one must understand, at the molecular level, how the energy associated with the work to overcome friction is converted to heat. Such knowledge is key to understanding the rate at which an interface will heat, and in addition how chemical reactions and other physical processes triggered by heat will be affected by friciton. One of the simplest possible geometries in which friction can occur, and thus be studied, is that of a fluid or crystalline monolayer adsorbed on an atomically flat surface. This geometry is experimentally accessible to experiments with a Quartz Crystal Microbalance (QCM), to numerical simulation techniques, and to analytic theory. A recent QCM experiment@footnote 1@ sought to explore the nature of electronic contributions to friction by measuring the friction associated with nitrogen monolayers sliding on Pb substrates as the temperature passed through the superconducting transition at 7.2K. The work inspired a number of subsequent theoretical and experimental efforts, which yielded contradictory results. A major complication associated with the Ref. 1 result arose from the fact that the data were reported for Pb substrates which had been exposed to air. We have thus repeated the measurements on Pb substrates which have been prepared in situ for both nitrogen and rare gas monolayers. The latter have been predicted by some theories to exhibit no dependence on the superconducting state of the sample. We present these results and compare them to the various conflicting theories. @FootnoteText@@footnote 1@ A. Dayo, W. Alnasrallah and J. Krim, Phys. Rev. Lett. vol 80, 1690 (1998) Work funded by NSF.

4:20pm **TR+MM-WeA8 Nanotribology of Total Joint Replacement Prosthesis (TJR)**, ***S.P. Ho,*** Clemson University; *R.W. Carpick,* University of Wisconsin - Madison; *T. Boland, P.F. Joseph, M. LaBerge,* Clemson University

Atomic force microscope (AFM) was used to represent nanotribological asperity-to-asperity nanocontact between a cast CoCr alloy and an unsterilized surgical-grade direct compression molded ultra high molecular weight polyethylene (UHMWPE) of TJR prosthesis. UHMWPE is a semicrystalline material consisting of crystalline domains within an amorphous matrix. The primary dependence of friction upon normal load during an abrasive nanocontact may involve gross plastic deformation leading to plowing of UHMWPE surface. We have studied the nanotribological properties and evolution of plastic deformation of UHMWPE, to determine the precursors to wear particle formation in TJR prosthesis. It was hypothesized that variability in friction due to the individual nano-constituents in the semicrystalline polymer could cause a stress concentration leading to the generation of nanoscale wear debris particle; the originator for osteolysis in a total joint arthroplasty. Results from AFM analyses will be presented in this work to elucidate the average coefficient of friction and wear mechanisms and to reveal friction coefficients of the individual nano-constituents in the UHMWPE. Results showed that loading the nanocontact within the elastic regime resulted in an average coefficient of friction of 0.25+/-0.04. Higher normal load ranges revealed a sudden increase in lateral force indicating ploughing of the nanocontact, eventually leading to generation of nanoscale wear debris. The sudden increase in lateral force indicated that the UHMWPE plastically deforms causing an increase in contact area leading to an increase in lateral forces. We will present data supporting the individual contribution of crystalline and amorphous regions to the coefficient of friction for the purpose of understanding the observed plastic deformation at the modeled nanocontact of total joint replacement prosthesis (TJR).

4:40pm **TR+MM-WeA9 Surface Force Dynamics and Nanotribology of Self-healing Monolayers Applied to MEMS Lubrication: A Study Using Dip Pen Nanolithography**, ***J.J. Nainaparampil,*** Systran Federal/MLBT, US; *K.C. Eapen,* UDRI/MLBT; *J.S. Zabinski,* AFRL/MLBT

Self-assembled monolayers (SAMS) have good potential for lubrication of microelectromechanical systems (MEMS). However, monolayers tend to wear away relatively quickly, which limits their usefulness. Mechanisms for monolayer replenishment have the potential to expand the role of SAMS in MEMS lubrication schemes. The dynamics of adhesion and friction forces of self-healing monolayer coatings is studied using techniques derived from dip pen nanolithography (DPN). Typically, DPN makes use of an Atomic Force Microscope (AFM) to write patterns with 'ink' that is deposited on the cantilever tip or delivered through a nanometric aperture.@footnote 1,2@ An AFM is used here to write monolayer patterns of various thiols, nonane dione and aminoalkylsilane on gold, copper, aluminum and silicon surfaces. Nanotribological measurements of adhesion and lubricity are measured using a combination of topography and lateral force scans. Special patterns that constrain molecular surface diffusion were used to permit studies of wear and replenishment dynamics. Measurements made on thiol and nonane dione monolayers on gold surfaces showed that stronger adhesion occurs for thiol coatings compared to nonane dione. The effects of relative humidity, temperature and aging on surface forces and monolayer dynamics will be presented. @FootnoteText@@footnote 1@Richard D. Piner, Jin Zhu, Feng Xu, Seunghun Hong and Chad A. Mirkin, Science 283, (1999) 661. @footnote 2@Mun-Heon Hong, Ki Hyun Kim, Joono Bae and Wonho Jhe, Appl. Phys. Lett. 77(16) (2000) 2604.

5:00pm **TR+MM-WeA10 Observation and Simulation of Dislocation Emission after Nanoindentation of an FCC (100) Surface**, *O. Rodríguez de la Fuente,* Universidad Complutense de Madrid, Spain; *J.A. Zimmerman,* ***J. de la Figuera,*** Sandia National Laboratories; *M.A. González,* Universidad Complutense de Madrid, Spain; *J.C. Hamilton,* Sandia National Laboratories; *J.M. Rojo,* Universidad Complutense de Madrid, Spain

The traditional use of indentation of materials to characterize mechanical hardness has benefited both from recent experimental and theoretical advances. The routine use of Scanning Probe Microscopes allows the detailed examination of the surface of materials after nanoindentation, using the same instrument for both deformation and analysis. Techniques used to model the defects generated during indentation have also advanced by the development of fast, parallel computations of million-atom systems governed by semi-empirical potential energy functions. Together, these advances are starting to bridge the gap between theory and experiment. We present a combined study of the emission of dislocation loops by indentation on the surface of Au(100) using Scanning Tunneling Microscope (STM) experiments and atomistic simulations employing the Embedded Atom Method (EAM). Our experiments show dislocation loops emitted in directions that extend out to distances hundreds of nanometers away from the indentation region. These loops consist of dissociated edge loops that intersect the surface. The locations of these dissociated loops are identified by the sub-angstrom height hillocks observed on the crystal surface. Atomistic simulation of nanoindentation reveals that these dislocation loops are generated close to the indentation region and glide away along directions. The sub-surface structure of the dislocation loops verifies the stacking faults beneath the hillocks, which intersect at a stair-rod dislocation. Our simulation permits an estimate of the Peierls barrier for loop glide, revealing why the dislocations can glide so far from the indentation region. We have also observed the same dislocation loops by annealing an ion-irradiated Au(100) surface. The atomistic simulations help to understand how the dislocation loops can withstand the annealing.

Vacuum Science & Technology
Room 125 - Session VST-WeA

Gas Sorption Phenomena II

Moderator: J.F. O'Hanlon, University of Arizona

2:00pm **VST-WeA1 Kinetic Parameters of Materials Outgassing: Experimental Determination Using Thermoelectric Quartz Crystal Microbalance**, *I. Gouzman, M. Murat,* ***E. Grossman,*** *Y. Noter, Y. Lifshitz,* Soreq NRC, Israel

The outgassing of polymer-based materials is a concern for all space-related applications. The knowledge of the kinetic parameters characterizing outgassing of materials is of great importance since they are used to predict the potential contamination and the associated degradation of space systems. In the present work thermoelectric quartz crystal microbalance (TQCM), incorporated in a modified ASTM E 595 standard outgassing system, was used to measure the kinetics of spacecraft materials' outgassing under high vacuum and elevated temperatures. The measurements were carried out by collecting the outgassed species on the TQCM sensor surface. The experimental procedure consisted of the following steps: (i) a stepwise increase of the sample temperature in the 25 - 125°C range, while keeping the TQCM at a constant temperature (25 or 0°C), (ii) cooling the sample and keeping it at room temperature without changing the TQCM temperature in order to isolate the contaminants re-emission process, and (iii) increasing the TQCM temperature in several steps, studying the effect of the temperature on the re-emission kinetics. An analytical model was developed to derive the outgassing and re-emission kinetic parameters from the experimental data. The system capabilities were demonstrated by studying the outgassing kinetics of several materials that included polysiloxane and polyurethane based black coatings (S2 and PU1, respectively, both manufactured by MAP, France) as well as a closed cell polymethacrylimide foam (Rohacell, manufactured by Rohm, Germany). Outgassing and residence times, activation energies, and the contamination potential of different components of the outgassed products were calculated based on the proposed model. The derived parameters can be used to predict the outgassing and contamination profiles of space systems, both on the ground (e.g. in a thermal vacuum tests) and in space.

2:20pm **VST-WeA2 UHV Compatibility of Organic Materials***, **M. Anderle,*** ITC-irst,, Italy*; C. Bellachioma, C. Benvenuti, E Broilo, S. Calatroni, P. Chiggiato, S. Clair, S. Elliott,* CERN, Switzerland*; J. Kenny,* University of Perugia, Italy*; W. Vollenberg,* CERN, Switzerland

Polymers and composite materials present many attractive properties for the construction of vacuum components. They are easily formed, light, robust and electrically non conducting. However, their use for UHV applications is hindered by an important outgassing of volatile elements contained in their bulk. Furthermore,they are also prone to gas permeation when exposed to a pressure difference. An obvious improvement strategy consists in coating them with a metallic thin film to produce a hybrid material which should combine the structural properties of a polymer with the vacuum properties of a metal. Along this line,various organic materials have been coated with thin films of different metals by sputtering. It has been found that the benefits hoped for could not be fully achieved due to pin-holes in the metal coating, which are a consequence of the presence of dust grains and morphology irregularities on the surface to be coated. A quantitatve analysis of the results indicates that the outgassing through the pin-holes is enhanced by lateral gas diffusion in the polymer material. The mathematical formulation of the process and the experimental results obtained to date are presented and discussed.

3:20pm **VST-WeA5 A Different View on the "Water Problem"***, **R.W. Dobrozemsky**,* Vienna University of Technology, Austria **INVITED**

Pumping times after air exposure with their strong implications on the economy of vacuum processes are mainly caused by the desorption of rather tiny quantities of water in vacuum systems. There is no doubt that, by reducing the adsorbed quantity or by shortening its sojourn time, faster pumping cycles could be achieved. The slow progress in this field is, among others, due to the lack of simple and quantitative methods for measurements of atmospheric water coverage and its kinetics. In order to find a method that exhibits the same sensitivity and accuracy in atmosphere as well as in vacuum, radioactive tracer technique has been studied with particular emphasis on tritium-tracer-technique (TTT). This method allows precise measurements of low coverage (down to 1 percent of a "monolayer" even on rather small samples) and of its kinetics over periods of several days. In addition, water coverage can be measured in a way that is not effected by other surface contaminants, or by shortcomings of usual vacuum gauges (sensitivity drift, outgassing, gas reactions on hot filaments, etc). Hitherto, atmospheric water adsorption on square-cm-sized samples of stainless steel, aluminum, silicone, gold, and glass has been studied. It was found that water adsorption depends highly on the cleanliness of the surface with no significant difference between stainless steel and gold. Furthermore, it turned out that sojourn times in vacuum are at least equal to or even much longer than those in atmosphere. Basic aspects of the method as well as experimental data will be discussed.

4:00pm **VST-WeA7 Effect of Readsorption in a Dynamic Vacuum System***, **P. Repa**, L. Peksa, T. Gronych,* Charles University, Czech Republic

Theoretical analyses of the pressure variations in vacuum chambers considering desorption and adsorption indicate that the time-pressure curves shall be modified by readsorption of the gases penetrating through or releasing from the walls.@footnote 1@. Nevertheless, no effect of readsorption was observed at some recent experiments@footnote 2-5@ which were curried out in sealed-off vacuum systems and the phenomenon has not been explained entirely yet. An aim of this work was to study an effect of readsorption on pressure variations in a dynamic vacuum system. Doses of several gases (H@sub 2@, CO, and H@sub2@O) were introduced into a uhv chamber of the apparatus that was simultaneously pumped. For the measurements, an apparatus was used that consist of a uhv chamber of volume 0,025 m@super3@ pumped by a uhv pump and a gas handling system enabling to vary a throughput of an introduced gas precipitously. The pumping speed of the pump could be set at values up to 0.1 m@super3@/s by a reduction valve. In the course of the measurements, the total and partial pressure vs. time curves were recorded at several selected pumping speeds. An analysis of the response of the pressure in the chamber to sudden variation of the throughput of the introduced gas implied that the influence of readsorption on the pressure behaviour was immeasurable small not only in the sealed-off but also in the dynamic vacuum systems as well. @FootnoteText@@footnote 1@Redhead P. A., J. Vac. Sci. Technol. A14, 2599 (1996). @footnote 2@Berman A. and Fremerey J. K. J., Vac. Sci. Tecnol., A5, 2436 (1987) @footnote 3@Bennett K. J. and Elsey R. J., Vacuum 44, 159 (1993) @footnote 4@Jousten K., Vacuum 47, 325 (1996). @footnote 5@Takeuchi K. at all, J. Vac. Soc. Japan 35 837 (1993) .

4:20pm **VST-WeA8 Influence of the Production Parameters on the Vacuum Properties of Ti-Zr-V Non-evaporable Getter Films***, C. Benvenuti, P. Chiggiato, C. Claeys, P. Costa Pinto, **A. Prodromides**, V. Ruzinov, I. Wevers,* CERN, Switzerland

Non-evaporable thin film getters of various composition have been produced by sputtering. Among about 20 materials which have been studied, the lowest activation temperature (about 180°C) has been displayed by a Ti-Zr-V coating obtained from a cathode made of intertwisted elemental wires. In order to optimize the vacuum properties of this coating, the production parameters have been varied, namely sputtering configuration (diode or magnetron), discharge gas, deposition rate, discharge voltage, substrate nature and temperature during coating. The films have been variously analysed by electron microscopy, electron stimulated desorption, ultimate pressure, pumping speed and rare gas degassing rate measurements. It has been found that the activation temperature, the pumping speed and surface capacity are strongly affected by the deposition rate and substrate temperature during coating. Optimum characteristics are obtained for high substrate temperatures (about 300 °C) and low deposition rates (about 0.15 µm/h).

4:40pm **VST-WeA9 Experimental Investigation of Impact-induced Molecular Desorption by 4.2 MeV/amu Pb Ions***, M. Chanel, J. Hansen, J.-M. Laurent, N. Madsen, **E. Mahner**,* CERN, Switzerland

In preparation for the heavy ion program of the LHC, accumulation and cooling tests with lead ion beams have been performed in the LEAR storage ring. These tests have revealed that due to the unexpected large outgassing of the vacuum system, the dynamic pressure of the ring could not be maintained low enough to reach the required beam intensities. To determine the actions necessary to lower the dynamic pressure rise an experimental program has been initiated for measuring the molecular desorption yields of stainless steel vacuum chambers by the impact of 4.2 MeV/amu lead ions with the charge states +27 and +53. The test chambers were exposed either at grazing or at perpendicular incidence. Different surface treatments are reported in terms of the molecular desorption yields for H@sub 2@, CH@sub 4@, CO and CO@sub 2@. Unexpected large values of molecular yields per incident ion up to 10@super 4@ molecules/ion have been observed. The implications of these results for the vacuum system of the future ion accumulator ring (LEIR) and possible remedies to reduce the vacuum degradation will be discussed.

Applied Surface Analysis
Room 134 - Session AS-ThM

Oxides and Oxidation

Moderators: D.R. Baer, Pacific Northwest National Laboratory, J. Haber, Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences

9:00am **AS-ThM3 Atomic Oxygen Irradiation of Polymers: Ground Simulation of LEO Environment***, **G. Lempert**, R. Intrater, I. Gouzman, E. Grossman, Y. Lifshitz,* Soreq NRC, Israel*; A. Hoffman,* Technion Haifa, Israel

External surfaces of spacecraft in low earth orbit (LEO) are exposed to the various constituents of the space environment, including atomic oxygen (AO) and solar UV radiation, which often compromise the material properties. Material degradation by LEO atomic oxygen is simulated in a variety of experimental facilities, each with their respective limitations. RF oxygen plasma is a widely used facility for screening materials for LEO application. In addition to the neutral oxygen atoms, the plasma generates electrons and ions as well as vacuum ultraviolet (VUV) radiation, which may also contribute, either directly or synergistically, to degradation of materials. In the present study, direct and synergistic degradation effects on polymers were investigated by exposing the polymers to various combinations of the different species and the VUV emanating from an RF oxygen plasma. The different exposure conditions, including AO alone, AO+VUV, AO+e@super -@+O@super +@+VUV, AO+e@super -@+VUV, AO+O@super +@+VUV, were separated downstream beyond the RF reactor exit. The samples were characterized by mass loss measurements, changes in surface composition, by XPS, and ATR-FTIR spectroscopy, and changes in surface morphology by AFM. The polymer samples investigated were, Kapton, fluorocarbons such as Teflon FEP, Tefzel and Tedlar, having different C/F ratios, and polyethylene. Fluorine containing polymers were confirmed to be more resistant to AO alone than hydrocarbons. However, fluorocarbon polymers, sensitive to VUV radiation, showed synergistic degradation effects and higher erosion yield under AO+VUV irradiations. The effect may be interpreted by VUV radiation induced scissioning, thereby facilitating the material erosion under AO attack. The results presented demonstrate the synergistic effects on the degradation of different polymer materials and elucidate the limitations of the validity of the common RF plasma for screening materials for LEO applications.

9:20am **AS-ThM4 Surface Oxidation on Pure Liquid InSn Alloy***, **M. Jenko**,* Institute of Metals and Technology, Slovenia

Fluxless vacuum soldering is widely used for hermetical encapsulation of image intensifier tubes and recently for miniature channel photomultiplier. Extremely clean surfaces are required to obtain good wetting at soldering process of this sophisticated sealing technique. An ultra thin oxide film, covering the liquid solder, can often cause leakage of fluxless soldering seals. The model study of pure indium oxidation in the temperature range from 20 to 400°C in a vacuum at 5x10@super -5@ mbar oxygen pressure was performed using in situ AES measurements. The formation of In@sub 2@O@sub 3@ in the temperature range from 20 to 360°C was established. At temperatures higher than 360°C isothermal dissociation of ultra thin In@sub 2@O@sub 3@ film on liquid In surface was found. We also studied the initial phases of surface oxidation on pure liquid InSn alloy (20at.% In, 80at.% Sn). The surface of liquid solder was exposed to pure oxygen at 250°C. On oxidized InSn surface (1,5 x 10 @super 5@L) only In@sub 2@O@sub 3@ was found. Thermodynamic calculations showed that a mixture of SnO, SnO and In@sub 2@O@sub 3@ was formed at these conditions. The mixed oxides appeared to be thermodynamic unstable near the alloy-oxide interface. The only stable oxide formed on the surface of liquid InSn alloy was found to be pure In@sub 2@O@sub 3@ at the temperatures of 250 ° and below 360°C. At higher temperatures (higher than 360°C) isothermal dissociation of ultra thin In@sub 2@O@sub 3@ on liquid InSn surface following by the process In@sub 2@O@sub 3@ (s)+ 4 In(l)= 3 In@sub 2@O (g) was established too.

9:40am **AS-ThM5 Oxidation of Scandium Layers on Tungsten***, **A. Shih**, J.E. Yater, C. Hor, R. Abrams,* Naval Research Laboratory

Scandate cathodes have demonstrated an emission density as high as 400A/cm@super 2@ at 1300 K. In order to develop a reliable fabrication technique for scandate cathodes, a thorough understanding of the surface chemistry involving Sc, Ba, O and W is essential. An initial approach is to investigate the interaction among the elements in subsets separately. In this study, Sc on W is studied by AES and TPD. The study reveals three states of Sc adsorption on W that originate from the first-, second- and multi ple-layer. It is desirable to incorporate metallic Sc in the fabrication because its high mobility is conducive to coating uniformity and to Sc replenishment. However, can metallic Sc survive the cathode activation process, which takes a few hours at 1500 K? The desorption-rate equation for the multiple-layer state has been determined as a function of the substrate temperature. At 1500 K, the evaporation rate is 40 µm/hour. Oxidation increases the binding energy of Sc. At 1500 K the evaporation rate of oxidized Sc is less than 0.04 layers/hour. Consequently Sc in the scandate coating should be in an oxidized form. We studied the oxidation process of Sc films and found that at room temperature oxygen has a very limited diffusion length in Sc films. In a 13-layer film after an exposure of 2000 L, 7 layers of Sc remains unoxidized. However, an elevated substrate temperature accelerates the oxidation process. For a 13-layer film, 3 layers and 1.5 layers of Sc remain un-oxidized after an oxygen exposure 48 L at substrate temperatures of 520K and 720K, respectively. This underlies the need of a thermal treatment of a scandate cathode in an oxidizing environment before activation.

10:00am **AS-ThM6 Mechanism of the Activation of Mg@sub 2@Ni for Hydrogen Up-Take by Surface Treatment With Liquid Water and Water Vapor***, **J.K. Lomness**, L.A. Giannuzzi, M.D. Hampton,* University of Central Florida

Magnesium nickel alloy (Mg@sub 2@Ni) has been considered an excellent hydrogen storage medium because it has a high hydrogen capacity, forms a very stable hydride, is inexpensive, and it presents no environmental hazards. One of the major problems associated with the use of magnesium nickel alloy for hydrogen storage is its activation for initial hydrogen uptake. Traditionally, high temperatures and high pressures are needed for initial activation of this alloy. It has been discovered that treatment of Mg@sub 2@Ni with liquid water and water vapor activates the alloy for hydrogen uptake. The purpose of this paper is to present results obtained from the surface modification of Mg@sub 2@Ni with liquid water and water vapor. The data obtained suggest the presence of a hydroxide on the surface. It is believed that this is the first report of the presence of hydroxides on the surface of an active hydrogen storage alloy. Data obtained from x-ray photoelectron spectroscopy and transmission electron microscopy will be presented.

10:20am **AS-ThM7 The Interaction of Organic Molecules with Oxidised Metal Surfaces: Studies by High Resolution XPS and ToF-SIMS***, J.F. Watts,*** University of Surrey, UK **INVITED**

The interaction of organic molecules with oxide surfaces is important in many areas of endeavor. At the University of Surrey we have been concerned with this phenomenon for more than two decades, and special emphasis has been applied in the arena of adhesion and adhesive bonding. Our work in this area has been concerned, predominantly, with adsorption from the liquid phase, and it will be shown that XPS and SIMS are ideally suited to the study of adsorption characteristics of such systems. This paper will review fundamental studies that have been undertaken with a view to providing guidelines that can be used in studies of organics on oxide surfaces in other spheres of interest. There are two basic parameters that must be addressed if we are to start to develop a model of the manner of interaction of an organic molecule with an oxide surface. The first is the capacity of the solid surface for the adsorbing molecule, the second is the nature of the bond that is formed between adsorbate and substrate. If the concern is of the behavior of very small amounts of adsorbing species, (up to a few monolayers, for example), there is also the concern regarding the conformation of the molecules and the degree of order in the adsorbed layer. In more complex situations the interest will be in the phenomenon of competitive adsorption where the adsorbing solution contains not one, but many potential adsorbates. Adsorption characteristics of substrates are readily deduced by the construction of adsorption isotherms based on XPS or ToF-SIMS data. In essence, once kinetic equilibrium has been found for a particular system, a series of measurements are made on the adsorption of organic molecules, from solution of various concentrations. The uptake curve, in the case of chemisorption, takes the form of a classical adsorption isotherm, and may be treated by procedures that reflect adsorption in accord with Langmuir, Temkin or other model as appropriate.

11:00am **AS-ThM9 Characterization of Rhenium Oxide Using ESCA***, **B. Panda**,* National Aeronautics and Space Administration

High melting point and inherent ductility (toughness) over a wide range of temperature has made Rhenium an engineering material of choice for several thrust chambers in propulsion systems. Although the material remains tough at high temperatures, it still can transform to several oxides. As many as eight different oxides have been reported in literature.@footnote 1,2@ When characterized using ESCA (Electron Spectroscopy for Chemical Analysis) these oxides show large shifts in the

Re 4f line positions. While this unique property could be used as a tool for oxide characterization, literature indicates that only a few of these oxides have been characterized.@footnote 3@ Current work focuses on characterizing oxides of Rhenium using ESCA. Spectral line (Re 4f) shifts have been measured for various oxides and the results have been compared with the line positions of real-time oxidation products from space hardware. @FootnoteText@ @footnote 1@ Druce,J. G. F. in "Rhenium", Cambridge, At The University Press, 1948,pp.29-35 @footnote 2@ Lebedev, K. B. in "The Chemistry of Rhenium", Translated by Ronson, L. and Woolf, A. A., Butterworths, London, 1962, pp. 13 -17. @footnote 3@ Broclawik, E., Haber, J., and Ungier, L. in "Electronic Structure of Rhenium Oxides" J. of Physics and Chemistry of Solids, Vol. 42, 1981, pp. 203 -208.

Biomaterials

Room 102 - Session BI-ThM

Protein Surface Interaction

Moderator: B.D. Ratner, University of Washington

8:20am **BI-ThM1 Physicochemical Properties of Polysaccharide Coatings as Determinants of Protein Adsorption***, P.G. Hartley,* CSIRO Molecular Science, Australia*; **S.L. McArthur,*** University of Washington*; K.M. McLean,* CSIRO Molecular Science, Australia*; S. Oiseth,* Chalmers University of Technology, Sweden*; G. Johnson, H.J. Griesser,* CSIRO Molecular Science, Australia **INVITED**

The use of protein resistant coatings has long been seen as a means of controlling the biological response to implanted materials. Whilst many such surfaces have been produced, the properties which give rise to their protein resistant character are often poorly elucidated. Polysaccharides have been frequently employed as surface modification agents in the biomaterials area by virtue of their ready availability and apparent protein repellancy. The ability to chemically derivatize polysaccharides is a further key feature which suits them to studies of the relationship between surface chemistry and protein adsorption. In our studies we have utilized this ability to produce a range of derivatized dextran coatings with variable physico-chemical properties. These properties have been characterized in detail using both aqueous and high vacuum surface analytical techniques. These results have then been correlated with the protein adsorption behaviour of the surfaces. The results highlight the interplay between surface charge and steric interactions in determining the protein selectivity and/or repellency of the polysaccharide surfaces. In addition, we have further correlated the surface properties with biological responses using in vitro cell adhesion and growth studies. These studies demonstrate that control over cellular responses may be achieved to a large extent by the manipulation of non-specific interactions between polysaccharide surfaces and extracellular matrix proteins.

9:00am **BI-ThM3 Effect of Adsorbate Alkyl Chain Length and Terminal Group Chemistry on the Adsorption of Fibronectin and Albumin on Self-assembled Monolayers***, **C.M.-J. Fauroux**, C.C. Dupont-Gillain, R.W. Manning,* UMIST, U.K.*; G.J. Leggett,* UMIST, U.K., UK

Recent studies of the responses of mammalian cells to self-assembled monolayers (SAMs) have provided important insights into the relationship between surface chemical structure and cell attachment to artificial surfaces. Our hypothesis is that a mechanistic explanation of the correlations we have observed depends upon a detailed knowledge of the composition of the protein layer that coats the SAM prior to cell attachment and the conformations of the molecules of which it is composed. Of particular importance are fibronectin (fn), which interacts with membrane receptors (integrins) involved in cell attachment, and albumin (alb), the must abundant component of serum but thought to inhibit attachment. We have studied the adsorption of these proteins onto a range of SAMs to determine whether there is a correlation between the results of our earlier studies and the kinetics of adsorption of these proteins. The kinetics of adsorption of single proteins (human alb and human fn) have been studied for methyl, hydroxyl and carboxylic acid terminated SAMs with short and long alkyl chains. Two complementary techniques have been used. Using @super 3@H-radiolabelling, the mass of adsorbed molecules per unit area may be determined. Measurement of the amide band intensity in Fourier transform infra-red spectroscopy (FTIR) also provides a measure of the amount of adsorbed protein. Data obtained by the two methods have been found to be in close agreement. It has been found that more alb adsorbed to methyl terminated SAMs than to carboxylic acid terminated SAMs, while the smallest amounts of adsorbed protein were observed for the hydroxyl terminated surfaces.

9:20am **BI-ThM4 Deformation of Proteins Adsorbed on Glass Surfaces as Characterized by XAS***, **H.E. Canavan,*** George Washington University*; J.J. Hickman,* Clemson University*; W.E. O'Grady,* U.S. Naval Research Laboratory*; D.E. Ramaker,* George Washington University

The interaction of proteins with artificial surfaces is of interest to many in the fields of medicine, biotechnology, and surface science. It is known that certain proteins experience considerable conformational deformation upon adsorption onto surfaces. In contrast, some proteins are described as colloidal or "hard," and experience little if any deformation upon adsorption. In the work presented here, the biomolecular interaction is characterized by X-Ray Absorption Spectroscopy (XAS). Sulfur K-edge XAS will be used to analyze the S-S, S-C and S-O bonds to monitor the extent to which the sulfur bond character is changed in both "hard" and "soft" proteins such as BSA, lysozyme, and cytochrome C upon their adsorption onto a glass surface. In addition, X-ray Photoelectron Spectroscopy (XPS) is used to characterize the glass surfaces both prior and subsequent to protein deposition.

10:00am **BI-ThM6 Reversible Adsorption/Desorption of Proteins from a Thermally Switching Polymer Monolayer***, **D.L. Huber,** M.A. Samara, B.C. Bunker, R.A. Manginell, C.M. Matzke, G. Dulleck,* Sandia National Laboratories

The phase transitions of poly(N-isopropyl acrylamide) (poly NIPAM) hydrogels have been studied extensively for a number of years. We have investigated the thermal transitions of the linear polymer bound to silicon oxide surfaces. The poly NIPAM monolayers are grown from a self assembled monolayer of free radical initiators, and their properties towards protein adsorption are studied as a function of temperature using IR and UV-visible spectroscopies, as well as ellipsometry and fluorescence microscopy. At room temperature, the monolayers are swollen with water and are extremely resistant to protein adhesion, but at elevated temperatures (above 35C) the polymer collapses and expels a large portion of the water. The collapsed polymer monolayers are capable of quickly adsorbing a protein monolayer. The layer of adsorbed protein can be completely desorbed by cooling the polymer to below its transition temperature. A well prepared monolayer has been shown to be capable of repeated adsorption and desorption cycles with no degradation of the effect. Poly NIPAM monolayers have been grown onto a microchip based platform containing micron scale resistive heaters capable of precisely controlling the surface temperature, and the adsorption and desorption of fluorescently labelled proteins monitored using flurorescence microscopy. Possible applications of on chip structures, as well as the adsorption/desorption kinetics will be discussed.

10:40am **BI-ThM8 Polyelectrolyte Multilayers : A New Tool to Design Targeted Biofilms***, **P. Schaaf,*** Institut Charles Sadron / Universite Louis Pasteur Strasbourg, France*; L. Szyk,* Unite INSERM U424 Strasbourg, France*; B. Tinland,* Institut Charles Sadron (CNRS) Strasbourg, France*; F. Cuisinier, P. Schwinte, J.C. Voegel,* Unite INSERM U424 Strasbourg, France

The alternate deposition of polycations and polyanions on a solid surface allows to build a polyelectrolyte multilayer film. This method whose driving force is the charge overcompensation at each adsorption step, offers a simple and elegand way to design new types of films with applications ranging from non linear optics to nanoreactors. The buildup procedure also offers the possibility to develop new bioactive films with multiple functionalities. One can, for example, easily embed proteins into these films. We will present results relative to this later aspect and in particular to the structure and the diffusion of proteins embedded in multilayers. It will be shown that proteins embedded in multilayers are not irreversibly fixed but can diffuse along the film. The diffusion coefficient depends upon the polyelectrolytes in contact with the protein. Such films seem also to preserve the secondary structure of the adsorbed and embedded proteins an even to enhance their thermal stability. Polyelectrolyte multilayers appear also to inhibit the formation of intermolecular beta-sheets frequently observed during the heating of protein solutions. Some new perspectives of these films for the coating of biomaterials will finally be presented.

11:00am **BI-ThM9 Design of Bioadhesive Polymers for Use at Mucosal Interfaces***, **A. Hoffman,*** University of Washington **INVITED**

Mucosal surfaces of the body include "wet" surfaces such as the eye, nose, mouth, GI-tract, vagina and lungs. They represent a large surface area of the body and thus may be an attractive route for delivery of drugs. When a drug formulation is applied to those surfaces, it may resist being washed away due to a combination of its own viscosity plus its intermolecular interactions with the mucous polymer coating. Two typical bioadhesive polymers that have been most often applied for mucosal drug delivery are polyacrylic acid and chitosan. This talk will describe drug delivery formulations containing PAA or chitosan or their derivatives that may provide better control over drug release rate and duration.

11:40am **BI-ThM11 The Role of Protein-surface Interactions in Implanted Joints***, M.R. Widmer, M. Heuberger, J. Voros,* ***N.D. Spencer****,* ETH-Zurich, Switzerland

Proteins appear to play an important role in the boundary lubrication of both natural and implanted hip and knee joints. However, the nature of the interaction of proteins in synovial fluid with the prosthetic tribosurface appears to influence the effectiveness of boundary lubrication significantly. Protein adsorption (waveguide and fluorescence experiments) and tribological (pin-on-disk) studies have been carried out on a number of polymer and model surfaces in order to determine the tribological role and nature of such interactions.

Electronics
Room 124 - Session EL-ThM
Quantum Electronics

Moderator: C.R. Abernathy, University of Florida

8:20am **EL-ThM1 Fabrication of a Silicon-based Solid State Quantum Computer***, R.G. Clark,* ***M.Y. Simmons****, A.S. Dzurak, A.R. Hamilton, S. Prawer, D.N. Jamieson, G. Milburn,* University of New South Wales, Australia **INVITED**

The fabrication of a scalable silicon-based quantum computer, in which the qubits are nuclear spin states of single phosphorus atoms embedded in isotopically pure silicon registered to surface control gates@footnote 1@, is a significant technological challenge. The Australian program is approaching this in two ways. In our ‘bottom up’ program the embedded phosphorus array is fabricated using advanced STM lithography techniques followed by Si MBE overgrowth. In our ‘top down’ strategy, a detailed process has been developed in which single phosphorus atoms are implanted (with on-chip verification) self-aligned to the surface control gates and fast single electron transistor readout devices. The fabrication pathways each have their list of associated problems. An outline will be given of the practical issues that have to be overcome, together with a view on how this might be achieved including progress to date. In our bottom-up program we have recently reported@footnote 2@ that it is possible to fabricate an atomically-precise linear array of single phosphorus bearing molecules on a silicon surface with the required dimensions for the QC. Our recent work has focused on the next step of implementing strategies for incorporating the P atoms substitutionally into the silicon surface with enhanced bonding and without disturbing the P array prior to encapsulation by subsequent silicon overgrowth. Our strategy in the top down program is to concentrate on fabricating the simplest few-qubit test structures that will enable us to access the critical physics. However we have approached this from the viewpoint of developing a reliable, reproduceable process which, for linear phosphorus arrays, can then be readily scaled up to multi-qubit devices. An overview will be given of key details of the top down fabrication scheme and measurements on the first test structures. @FootnoteText@ @footnote 1@ B.E.Kane, Nature 393, 133 (1998) @footnote 2@ J.L. O ’Brien, S.R. Schofield, M.Y. Simmons, R.G. Clark, A.S. Dzurak et al, Phys. Rev. B Rapid Communications (in press): cond-mat/0104569 (2001)

9:00am **EL-ThM3 Ratchets, Heat Pumps and Maxwell's Demon: Quantum Transport in the Non-linear Regime***,* ***H. Linke,*** Univ. of Oregon, Eugene*; T.E. Humphrey,* Univ. of New South Wales, Australia*; P.E. Lindelof,* Niels-Bohr Inst., Denmark*; A. Lofgren,* Lund Univ., Sweden*; R. Newbury,* Univ. of New South Wales, Australia*; P. Omling, W.D. Sheng,* Lund Univ., Sweden*; A.O. Sushkov,* Univ. of New South Wales, Australia*; A. Svensson,* Lund Univ., Sweden*; R.P. Taylor,* Univ. of Oregon, Eugene*; H.Q. Xu,* Lund Univ., Sweden **INVITED**

Ratchets are non-equilibrium systems in which directed particle motion is generated using spatial or temporal asymmetry, in the absence of time-averaged macroscopic forces or gradients. After introducing general examples for ratchets and their application s, an overview will be given on a series of recent experiments on so-called quantum ratchets for electrons. These devices are based on GaAs/AlGaAs heterostructures containing a two-dimensional electron gas. The non-linear response of a spatially asymmetri c nanostructure (such as a triangular quantum dot) to an applied voltage is used to partially rectify a symmetric AC voltage. The required non-linear behaviour is generated using quantum effects, such as electron interference or tunneling through an asymm etric energy barrier. A particularly interesting observation is that the direction of the current generated in tunneling ratchets depends on energy, that is, the net flow of electrons at low energy is in a direction opposite to that of electrons at highe r energy. This observation implies that quantum ratchets perform an energy-sorting task similar to that assigned to Maxwell's demon - that is, they may act as heat pumps or even as heat engines. We will discuss the properties of such quantum heat pumps, focusing the discussion on the thermodynamic limits to their efficiency.

9:40am **EL-ThM5 Two Dimensional Electronic Properties of a Disordered Three Dimensional Conductor in the Extreme Quantum Limit***,* ***D. Haude,*** *M. Morgenstern, I. Meinel, R. Wiesendanger,* Hamburg University, Germany

Scanning tunneling spectroscopy images of n-InAs(110)are recorded in magnetic fields corresponding to the extreme quantum limit. From the results it is concluded that the appearence of the so called Hall dip in magnetotransport corresponds to an appearance of a contrast pattern in the local density of states. The energy and magnetic field dependence of the contrast pattern is very similar to drift states usually expected in two dimensional systems exhibiting the quantum Hall effect. The appearance of a pseudogap at the Fermi level evidences that localization is involved in the change of the local density of states. From the results a simplified but straightforward explanation of the Hall dip controversially discussed since 1956 can be given.

10:00am **EL-ThM6 First-principles Study of Conduction Channels of Atomic Wires***, N. Kobayashi,* National Institute of Advanced Industrial Science and Technology (AIST), Japan*; M. Aono,* Osaka University, Japan*;* ***M. Tsukada****,* University of Tokyo, Japan

Electron transport through nanoscale structures has been investigated from the viewpoint of nanoscale physics and technology. A number of studies have been performed for the transport of atomic wires and molecular bridges. One of the theoretical approaches to the transport is analysis of individual conduction channels. We report an analysis of the conduction channels of atom wires using the density functional theory with nonlocal pseudopotentials. Electronic states are calculated using the Green function technique, and are decomposed into individual channel components using the eigenchannel decomposition. We elucidate the channel transmission, the channel local density of states, and the channel current density, and clarify the characteristics of the channel for material kind. Furthermore, we show how the channels open or close for finite bias voltage, and discuss the I-V characteristics.

10:20am **EL-ThM7 Quantum Transport through One Dimensional Aluminum Wires***,* ***I.P. Batra****, P. Sen, S. Ciraci,* University of Illinois at Chicago

Quantum conductance and quantized Hall resistance in narrow channels have been well understood by using the two-dimensional electron gas (2DEG), a model system which has been realized in semiconductor heterojunctions. An essential property of the 2DEG is its ability to produce a constriction of width comparable to the Fermi wavelength, a property not shared by even thin metal films. But the advent of scanning tunneling microscopy (STM) has enabled scientists to fabricate wires of "atomic" dimensions. This has led to an explosion of interest in the quantum transport properties of nanostructures. Here we consider the specific case of a one dimensional (1D) wire consisting of Aluminum atoms. First we have to find the optimal structural arrangement of the 1D system. This was done using the first-principles density functional method combined with molecular dynamics. It is found that aluminum can form stable zigzag structures similar to those found for Au. In addition, we find, other novel structures, which have not been reported for any other material. We present our understanding of the bonding as derived from charge density analysis for aluminum wires. With the calculated atomic and electronic structure in hand we proceed to discuss the quantum ballistic transport through these nanowires. Our calculations are based on channel capacity arguments that can be motivated using the Heisenberg's uncertainty principle. Our results are compared with the numerical calculations by Lang, who has performed careful analysis of conductance as a function of Al nanowire length in atomic domain. We finally comment on the thermal conductance and Wiedemann-Franz law in the nano-domain.

10:40am **EL-ThM8 Probing a One Dimensional Conductor Confined Below a Charged Step Edge***, **Chr. Meyer**, M. Morgenstern, J. Klijn, R. Wiesendanger,* Hamburg University, Germany

Although one dimensional conductors exhibit unique properties, spatially resolved investigations are still rare. On InAs(110) we found a special type of charged step edge inducing a one dimensional electron system (1DES) below that step edge. We investigated this quantum wire with scanning tunneling spectroscopy (STS) over a length of 800 nm in various magnetic fields between 0 T and 6 T. The STS-curves on the step edge show two subbands of the 1DES with ground state energies of -66 meV for the first and -20 meV for the second subband giving an electron density of 1.2x10@super 8@/cm. Spatially resolved images of the local density of states (LDOS) reveal that the first and second subband have a width of 20 nm and 50 nm respectively. Along the step edge the LDOS of the 1DES shows an energy dependent fluctuation length in the range from 15 nm to 70 nm corresponding to the dispersion of InAs. We suggest that electron scattering on impurities in the quantum wire is responsible for the observed fluctuations in the LDOS. We compare our measurements with theoretical calculations of a random field disordered 1DES, that predict a broadening of the ideal 1D DOS.

Magnetic Interfaces and Nanostructures
Room 110 - Session MI+NS-ThM

Magnetic Imaging and Spectroscopy

Moderator: P.N. First, Georgia Institute of Technology

8:20am **MI+NS-ThM1 Measurement of Spin Polarization using Andreev Reflection***, **R.J. Soulen**, M.S. Osofsky, G. Trotter,* Naval Research Laboratory **INVITED**

Measurement of spin polarization using Andreev reflection A new class of electronics is emerging which relies on the ability of ferromagnetic materials to conduct spin polarized currents. The performance of devices based on this phenomenon is greatly enhanced as the spin polarization, P, of the ferromagnetic material approaches 100%. In the face of difficulties in measuring this important property, we have developed a very simple method to determine P in which a superconducting point is placed in contact with the candidate ferromagnetic material. The Andreev reflection process at the interface between the two metals is influenced by the spin polarization of the ferromagnet enabling the determination of P through measurement of the conductance of the contact. In a very short time we have been able to measure the spin polarization of several metals and conducting oxides: NixFe1-x; Ni. Co, Fe, NiMnSb, La0.7Sr0.3MnO3; CrO2, whose spin polarization ranges from 25% to over 90%. Our results compare well with other magnetic spectroscopy measurements of P where available. Our search continues for a material with 100% spin polarization.

9:00am **MI+NS-ThM3 Point Contact Spectroscopy in Magnetic Fields***, **M. Tsoi**,* IBM Almaden Research Center **INVITED**

9:40am **MI+NS-ThM5 Magnetocrystalline Anisotropy Probed using X-ray Magnetic Linear Dichroism***, **S.S. Dhesi**,* ESRF, France*; G. van der Laan,* Daresbury Laboratory, UK*; E. Dudzik,* Hahn-Meitner-Institut, Germany*; A.B. Shick,* University of Davis, California

The anisotropy of the spin-orbit interaction,@lambda@@sub 2@, in vicinal Co films has been measured using x-ray magnetic linear dichroism (XMLD). A linear increase in @lambda@@sub 2@ with Co step density is found using a new sum rule and represents the first experimental confirmation that XMLD probes the magnetocrystalline anisotropy energy (MAE). X-ray magnetic circular dichroism (XMCD) is used to confirm that the XMLD arises from changes in the local step-edge electronic structure. The XMLD sum rule gives a larger MAE compared to macroscopic values and is discussed with respect to other local probes of the MAE.

10:00am **MI+NS-ThM6 Soft X-ray Microscopy to Image Magnetic Domain Structures at High Resolution***, G. Schuetz,* Universitat Wurzburg, Germany*; **P. Fischer**,* MPI-MF, Germany **INVITED**

X-ray magnetic circular dichroism (X-MCD) serves as huge element-specific magnetic contrast mechanism in combination with soft X-ray microscopy to image magnetic domains with a current lateral resolution down to 25nm. The sensitivity of X-MCD on the projection of the magnetization of the ferro(i)magnetic species along the photon propagation direction allows to study both in-plane and out-of-plane magnetized systems. The capability of this photon based microscopy to record the images in varying external magnetic fields and the high sensitivity down to thicknesses of a few nm is outlined and proofs this novel technique to be a promising tool for the study of the switching behaviour of individual layers in thin film magnetic media that are currently discussed (magnetic sensors, spintronic devices, etc.). Recent results obtained on nanostructured and multilayered systems will be presented together with micromagnetic simulations to get insight into the micromagnetic properties of these systems.

10:40am **MI+NS-ThM8 Photoemission Electron Microscopy and X-Ray Magnetic Circular Dichroism of Ultrathin FeNi Alloy Films on Cu(111)***, **Y. Sato**, T.F. Johnson, S. Chiang,* University of California, Davis*; F. Nolting, A. Scholl,* Lawrence Berkeley National Laboratory*; X.D. Zhu, D.P. Land,* University of California, Davis

We are studying the system of NiFe/Cu(111) to understand and control the surface/interface magnetism relevant to the application of the giant magnetoresistive effect to magnetic recording heads. We used the Photoemission Electron Microscope (PEEM2) at the Advanced Light Source to observe the domain structures of the alloy films. PEEM has the unique capability of imaging the film's magnetic structure with high spatial resolution and elemental specificity. Element specific magnetic contrast images and X-ray Magnetic Circular Dichroism (XMCD) spectra were obtained for eight different samples of varying Fe compositions at two different thicknesses. Samples with higher Fe content (x = 0.66, 0.74) were non-magnetic at room temperature. This trend of reduction in Curie temperature at higher Fe concentration agrees both with our XMLD data on the same system@footnote 1@ and with previous work on FeNi/Cu(100).@footnote 2@ We speculate this is a structure-driven effect related to the "Invar effect" in the bulk alloy. The PEEM images clearly show that Fe and Ni form a good alloy and have the same domain structures with their magnetization aligned. Further, we find a strong thickness and concentration dependence of the magnetic domain structures. For 5ML films, the domain structures appear to be strongly influenced by surface topography of the substrate. For 10ML films, however, the effect of the substrate features is already insignificant. At this thickness, the Fe concentration is also found to affect the size of the domains and the presence of an easy magnetization axis. @FootnoteText@ @footnote 1@T.F.Johnson, S.Chiang, Y.Sato, et al., to be published @footnote 2@F.O.Schumann, S.Z.Wu, G.J.Mankey and R.F.Willis Phys.Rev.B 56, 2668 (1997).

11:00am **MI+NS-ThM9 Imaging Magnetization in MRAM Elements with Soft X-Ray Microscopy***, **J.B. Kortright**, G. Meigs, G.P. Denbeaux,* Lawrence Berkeley National Laboratory*; J.M. Slaughter, R. Whig, S.-I. Han,* Motorola

The magnetic elements used to store information in MRAM devices will have dimensions of less than 1 micron laterally and roughly 5 nm in thickness. Such small dimensions make it difficult to directly observe field-dependent magnetization structure in individual elements, and possible interactions between elements, by conventional magnetic microscopy techniques. We are using scanning and imaging soft x-ray microscopes based on zone-plate lenses (with resolution approaching 30 nm) and resonant magnetic circular dichroism contrast to image magnetization structure during reversal in arrays of lithographically patterned bits on SiNx membrane substrates. Remnant magnetization structure and its evolution through reversal are clearly resolved, as is the dependence of this structure on element size, shape and cyclic reversal. Following a brief review of techniques, microscopy results relevant to MRAM applications and comparisons with micromagnetic theory will be presented. Work at LBNL was supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. Work at Motorola Labs was partially funded by DARPA.

11:20am **MI+NS-ThM10 Imaging Magnetic Nanostructures by Spin-Polarized Scanning Tunneling Microscopy***, **M. Bode**, A. Kubetzka, O. Pietzsch, M. Kleiber, R Ravli@aa c@, R. Wiesendanger,* University of Hamburg, Germany **INVITED**

Our recent progress in spin-polarized scanning tunneling microscopy (SP-STM) will be reviewed. By using magnetic thin film tips and spectroscopic techniques we could image the surface spin-structure of different surfaces and ultrathin films with a spatial resolution down to the atomic level. Namely, we will present results obtained on the topological antiferromagnet Cr(001),@footnote 1@ on self-organized Fe-nanowires@footnote 2@ and -islands,@footnote 3@ and on the antiferromagnetic monolayer of Mn/W(110).@footnote 4@ We will demonstrate that in-plane and out-of-plane spin-contrast can be achieved by choosing appropriate magnetic tip coatings and that the use of an antiferromagnetic tip material avoids any influence of the tip´s magnetic stray field on the sample´s domain structure. In contrast to most other electron-based microscopic techniques SP-STM as a near-field method can be applied even in large external magnetic fields up to several Tesla allowing the investigation of hysteresis effects in magnetically hard materials. @FootnoteText@ @footnote 1@ M. Kleiber et al., Phys. Rev. Lett. 85, 4606 (2000).@footnote 2@ O. Pietzsch et al., Phys. Rev. Lett. 84, 5212 (2000).@footnote 3@ A. Kubetzka et al., Phys. Rev. B 63, 140407 (2001). @footnote 4@ S. Heinze et al., Science 288, 1805 (2000).

Microelectromechanical Systems (MEMS)
Room 130 - Session MM-ThM
Characterization of MEMS Materials

Moderator: C.A. Zorman, Case Western Reserve University

8:20am **MM-ThM1 Mechanical Properties of MEMS Materials***, **W. Sharpe**,* Johns Hopkins University **INVITED**

The "mechanical" part of "microelectromechanical systems" (MEMS) requires knowledge of mechanical properties to predict relations between forces and displacements. Young's modulus and Poisson's ratio are needed for elastic response, and the strength of the material is needed to determine the allowable forces or displacements. Tensile testing is the preferred approach for structural materials because its uniform stress and strain fields enable direct determination of mechanical properties according to their definitions. Tensile testing of small thin-film specimens presents three challenges - preparation and handling of the specimen, measurement of small forces, and measurement of strain in the specimen. The author and colleagues at Hopkins have developed techniques and procedures for tensile testing of polysilicon, silicon nitride and silicon carbide. It is easier to measure mechanical properties of MEMS materials indirectly by modeling microdevices and extracting properties. One can fabricate a comb-driven resonant structure and use the measured resonant frequency to determine the modulus. Thin membranes of different shapes can be pressurized, and the measured displacements used to determine both Young's modulus and Poisson's ratio. Cantilever or fixed-end beams can be deflected electrostatically to measure modulus. However, none of these indirect approaches permit measurement of all the three properties (modulus, ratio, strength) simultaneously as does the tensile test. This presentation summarizes the current state-of-the-art in terms of test methods and the values of the polysilicon and other materials used in MEMS.

9:00am **MM-ThM3 The Beam vs. Plate Distinction for Si Strips Mechanically Loaded in Bending***, **S.K. Kaldor**,* Columbia University*; I.C. Noyan,* IBM T.J. Watson Research Division

Silicon structures used in microelectromechanical systems (MEMS) are generally anisotropic and possess dimensions that make it difficult to determine whether a beam or plate solution is more appropriate. Since a plate has an increased stiffness over that of a beam, errors of up to 10% in predicted displacements and stresses can occur if the proper bending solution is not employed. For single crystal Si samples loaded in four-point bending, we report both finite element modeling results and x-ray curvature measurements that illustrate the effects of boundary conditions (bending jig rollers used to apply displacements), specimen anisotropy, and specimen dimensions. We find that the transverse, or anticlastic, bending effects, which are ignored by 2-D solutions, should be considered as they can result in non-uniform loading across the sample width, and they are important in deciding whether a beam or plate solution should be used. While the sample's width-to-thickness ratio is typically the only criterion used to differentiate between beam and plate structures, we show that it is necessary to consider not only the sample's width and thickness but also the amount of applied bending; this was first considered by Searle@footnote 1@ in 1908. We show that the Searle parameter, width@super 2@/(thickness * bending radius), can be used to accurately differentiate between beam and plate structures. Furthermore, the difference in stiffness between a beam and a plate depends on the Poisson's ratio of the bent material. Since Poisson's ratio in Si can vary from 0.06 to 0.36 with crystallographic orientation, controlling the bending direction of a single crystal is a possible method for tailoring the specimen's flexural rigidity. @FootnoteText@ @footnote 1@ G.F.C. Searle, "Experimental Elasticity," 2nd ed. Cambridge UP, 1920.

9:20am **MM-ThM4 Amorphous Diamond MEMS***, **J.P. Sullivan**, T.A. Friedmann, M.P. de Boer, M.T. Dugger, M. Mitchell, R.G. Dunn, R. Ellis,* Sandia National Laboratories*; D.A. LaVan,* Massachusetts Institute of Technology

Microelectromechanical systems (MEMS), including electrostatic comb drives, simply-supported beams, and tensile test specimens, have been fabricated from amorphous diamond (aD), a pure carbon material with mechanical properties similar to crystalline diamond. Measurements using aD MEMS revealed that the material has high strength (8 GPa), fracture toughness (8 MPa.m@super 1/2@), and elastic modulus (800 GPa). These properties, combined with good inherent wear resistance, makes the material useful for achieving long lifetime MEMS that have rubbing surfaces or experience impact loading. Hydrophobicity and bio-compatibility of aD were also evaluated. The water contact angle was found to range from 84° for the as-prepared MEMS material up to 94° after annealing to 850°C. The increase in contact angle with annealing is similar to that found for crystalline diamond surfaces, which is due to O desorption that leaves an H-terminated surface. The hydrophobic nature of aD greatly reduces stiction in MEMS, thus permitting release without the use of applied hydrophobic coatings or supercritical drying. Bio-compatibilty was tested through the use of cultured cell growth, using bovine capillary endothelial cells, on bare and fibronectin-coated aD surfaces. Limited cell growth and adhesion was found for the uncoated aD surface, while good growth and adhesion was found for the fibronectin-coated aD. This is desirable for the creation of bioMEMS. Finally, the very high elastic modulus of this material is desirable for achieving mechanical structures with high resonant frequency. A key requirement for mechanical oscillators used for electrical signal processing is the need for high quality factor, Q. The Q for aD MEMS oscillators operating in vacuum will be reported and compared to that found for silicon oscillators. Sandia is a multiprogram lab operated by Sandia Corp., a Lockheed Martin Co., for the U.S. D.O.E. under contract DE-AC04-94AL85000.

9:40am **MM-ThM5 Fabrication Techniques and Integration Processes for a New Ultrananocrystalline Diamond (UNCD) -Based MEMS Technology and Characterization of UNCD Mechanical Properties***, **O. Auciello**, A.V. Sumant, D.M. Gruen, J.A. Carlisle, J. Birrell, N.A. Moldovan, D.C. Mancini, M. Angadi,* Argonne National Laboratory*; H.D. Espinosa, B.C. Prorok,* Northwestern University

State-of-the-art Si-based MEMS components exhibit serious performance limitations due to the relatively poor mechanical and tribological properties of Si. Diamond and diamond-like materials are investigated for MEMS applications, but they also have microstructural /properties, and/or processing limitations. A novel diamond coating technology developed at ANL yields phase-pure UNCD coatings with 2-5 nm grains and smooth surfaces,in addition to hardness of 97 GPa and friction coefficient of ~ 0.01, both similar to pure diamond. The unique growth process (involving C60 or CH4 /Ar microwave plasmas), based on C2 dimer insertion into the growing film, results in low activation energy for growth of UNCD on various substrates down to a record low temperature of ~350 °C. We demonstrated the fabrication of high-resolution UNCD-based 2-D and 3-D MEMS components, such as micro-gears, pinwheels,cantilevers, strain-gauges, and a microturbine, via growth of UNCD on Si and sacrificial SiO@sub 2@ layers, and selective etching. UNCD coatings can be grown conformally on high aspect ratio Si structures. UNCD coatings exhibit excellent mechanical and tribological properties, in addition to extremely low threshold voltage for electron field emission, which allows to produce MEMS sensors using the uniquely combined mechanical/electron emission properties of UNCD. We will discuss fabrication issues and UNCD properties applicable to MEMS. Work supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38.

10:00am **MM-ThM6 Silicon Carbide Films by Low Temperature CVD for MEMS Applications***, **D. Gao**, C.R. Stoldt, W.R. Ashurst, C. Carraro, R. Maboudian,* University of California, Berkeley

The single source CVD precursor, 1,3-disilabutane, is used to grow polycrystalline cubic silicon carbide (SiC) films for MEMS applications at temperatures below 1000 C. Using this process, SiC films are integrated into surface and bulk micromachining technologies to obtain SiC-based micromechanical structures. SiC cantilever beam arrays and strain gauges are fabricated and used to characterize film stress and stress gradients. Also, released polysilicon microstructures are coated with thin SiC films, and exhibit superior physicochemical characteristics. For instance, SiC-coated lateral resonators are functional after HF and hot KOH treatments and display increased resonant frequencies.

10:20am **MM-ThM7 Thermal Characteristics of Microswitch Contacts*, X. Yan*,** *N.E. McGruer, G.G. Adams,* Northeastern University*; S. Majumder,* Analog Devices, Inc.

Electrostatically actuated microswitches and relays developed at Northeastern University are approximately 100 x 100 µm in size and have been tested beyond 10@super 9@ cycles with a current of 2 mA per contact. For gold-gold contacts, the microswitches fail in a permanently closed mode in less than 10 cycles for currents exceeding 300 mA. At currents of approximately 1 A, the drain electrode melts, resulting in a permanently open switch. A number of authors have reported on various aspects of heat conduction through larger contacts. Hyman and Mehregany have discussed the contact physics of microcontacts, and modeled their thermal behavior.@footnote 1@ However, they do not consider the effect of the thin film traces leading up to the contacts in most MEMS switch designs. Finite element modeling and experiments have been used to study the thermal characteristics of microswitches. Because of the asymmetry in the contact geometry, the highest temperature is located in the thin film contact trace rather than at the contact interface. Contributions from convection and radiation are negligible, and conduction through the gas is marginally important. The hottest spot moves away from the contact as the contact radius increases, from 0.3 µm for a 100 nm contact radius to 2.7 µm for a 500 nm contact radius. Measurements show a sharp decrease in the contact resistance at a switch voltage of about 0.08 V and a current of 0.15 A, which may be due to softening of the contact surfaces and/or removal of surface contaminants. The result is in rough agreement with the onset of softening predicted by the model. The contact trace melts at a switch current of 1 A. The melted region is between 3.5 and 6 µm away from the center of the contact, slightly further than is predicted by the model. @FootnoteText@ @footnote 1@Daniel Hyman and Mehran Mehregany, Proc. of 44th IEEE Holm Conf. on Electrical Contacts (Arlington, VA, October 26-28, 1998, pp.133-140).

10:40am **MM-ThM8 MBE-grown Single-crystal Ferromagnetic Shape Memory Ni@sub 2@MnGa Thin Films*, J.W. Dong*,** *J. Lu, J.Q. Xie, Q. Pan, J. Cui, S. McKernan, R.D. James, C.J. Palmstrom,* University of Minnesota

Ni@sub 2@MnGa is a ferromagnetic shape memory alloy which goes through a thermodynamically reversible martensitic phase transformation and demonstrates ferromagnetic properties. In bulk, Ni@sub 2@MnGa with the stoichiometric composition has a Curie temperature ~376 K and the martensitic phase transformation occurs ~202 K. Above 202 K, Ni@sub 2@MnGa adopts a cubic L2@sub 1@ crystal structure with weak magnetic anisotropy. Below 202 K, it will transform to a tetragonal structure with greatly enhanced magnetic anisotropy. In this low-symmetry tetragonal phase, a twinning structure will be formed by three types of martensitic variants with different magnetic easy axes. External magnetic and/or stress fields can be employed to adjust the volume fraction of the twinned martensitic variants by the motion of twin boundaries. This will result in large reversible strain and this novel mechanism is thus called ferromagnetic shape memory effect. In bulk single crystals of Ni@sub 2@MnGa, strain as large as 6.1% has been demonstrated. This makes it a promising candidate for magnetic field driven actuator material. For micro-electro-mechanical-system (MEMS) actuators, conceptual designs based on single-crystal Ni@sub 2@MnGa films have been proposed. The first single-crystal growth of Ni@sub 2@MnGa thin film has been reported by the authors.@footnote 1@ The 300 Å-thick film grows pseudomorphically on a (001) GaAs substrate with a unique tetragonal structure (a = b = 5.65 Å, c = 6.12 Å). The Curie temperature was measured to be ~320 K. Moreover, martensitic phase transformation is observed in a partially released 450 Å-thick epitaxial film. In this presentation, we will report the growth, characterization, and patterning of 900 Å-thick single-crystal Ni@sub 2@MnGa films to elucidate the concept of using it in MEMS actuators. @FootnoteText@ @footnote 1@ J.W. Dong, L.C. Chen, C.J. Palmstrom, R.D. James, and S. McKernan, Appl. Phys. Lett., 75, pp. 1443-1445 (1999).

11:00am **MM-ThM9 Stability of Alkylsilane Monolayer Films in Humid Environments*, T.M. Mayer*,** *H.I. Kim, M.G. Hankins, M.P. de Boer,* Sandia National Laboratories

Alkylsilane monolayer films on SiO@sub 2@ are used to prevent adhesion in micromechanical (MEMS) devices. We have studied the stability of these films in humid environments, where degradation may lead to loss of hydrophobic character, water adsorption, and adhesion of MEMS components by capillary condensation. In this work we study silane monolayer films with both fluorocarbon and hydrocarbon side chains, deposited by both solution and chemical vapor deposition methods. In-situ ellipsometry and interfacial force microscopy measurements examine water vapor adsorption and its effect on adhesion and friction. Ex-situ atomic force microscopy and x-ray reflectivity measurements examine the morphology and density of the films before and after exposure. We find that chemical binding of the film to the surface is critical for its stability. Silanol films are not strongly bound to the surface and exhibit substantial water adsorption. This is accompanied by an irreversible increase in friction when probed with a similarly functionalized tip. In the presence of high humidity at room temperature, the silanol film restructures to form small droplets on the surface, leading to increased adhesion in cantilever beam MEMS test structures. In contrast, silanol films that have been annealed to react with surface hydroxyls are strongly bound to the surface and display negligible water adsorption, no effect on adhesion or friction, and no surface restructuring after exposure to high humidity (>80% RH) for short periods (10 hr) at room temperature. Stability of these films after more severe exposure (longer times at higher temperature), mechanisms of degradation, and long-term effects on the performance and reliability of MEMS devices will be addressed. Sandia is a multiprogram laboratory operated by Sandia Corp., a Lockheed Martin Company, for the U. S. Dept. of Energy under contract DE-AC04-94AL85000.

Nanotubes: Science and Applications Topical Conference
Room 133 - Session NT+EL+NS-ThM

Nanotubes: Growth, Functionalization, and Sensors

Moderator: P.M. Ajayan, Rensselaer Polytechnic Institute

8:20am **NT+EL+NS-ThM1 Control of Carbon Nanofiber Growth: "Base" versus "Tip" Growth Regimes*, A.V. Melechko*,** University of Tennessee*; V.I. Merkulov,* Oak Ridge National Lab*; M.A. Guillorn,* University of Tennesse and Oak Ridge National Lab*; D.H. Lowndes,* Oak Ridge National Lab*; M.L. Simpson,* University of Tennesse and Oak Ridge National Lab

Carbon nanofibers (CNF) show promise for many applications in such new areas as nanoelectronics and nanobiotechnology. It is very important to have a precise control of the position, orientation, and shape of the CNFs to maximize their utility for these applications. Recently it became possible to achieve such deterministic growth by nanopatterning catalyst and using Plasma Enhanced Chemical Vapor Deposition (PECVD). PECVD is a complex process that involves control of many interdependent parameters such as pressure, mass flow ratio (C2H2/NH3), substrate temperature, substrate material, plasma intensity and bias. Two different CNF growth regimes have been observed. One is when the catalyst particle is detached from the substrate surface and located at the tip of the CNF ("tip-growth" regime). Another regime is when the catalyst particle stays attached to the substrate ("base-growth" regime). We present an experimental study of the parameter space of a DC PECVD process for different regimes of CNF growth: "base-growth", "tip-growth", and intermediate regimes, where both types of CNFs were observed simultaneously. The mechanisms, which are responsible for the competition of these different growth phases, such as catalyst-substrate interaction and interdiffusion, formation of amorphous carbon film, and kinetics of catalysis and carbon diffusion through catalyst particle will be discussed.

8:40am **NT+EL+NS-ThM2 Scanning Tunneling Microscopy and Spectroscopy of Gd@@C@sub 82@-filled Single-walled Carbon Nanotubes***, J. Lee,* Seoul National University, Korea*; J.-Y. Park,* Cornell University*;* ***H.J. Kim****, H. Suh,* Seoul National University, Korea*; Y. Kuk,* Seoul National University, Korea, South Korea*; H. Kato, T. Okazaki, H. Shinohara,* Nagoya University, Japan

In this presentation we will show the atomic resolution STM images of single-walled carbon nanotubes filled with Gd@@C@sub 82@ metallofullerenes at ~7K. Atomic resolution images of Gd@@C@sub 82@-filled SWNTs with small tip bias voltages show nanometer-scale variations in topographic height and in atomic-scale corrugation pattern along the longitudinal axis of the nanotube. In the image with larger tip bias voltage of -1V, we could clearly observe the randomly oriented protrusions spaced roughly by integer multiples of 1.1nm which corresponds to the spacing between metallofullerenes in the nanotube. It is thought that the protrusions are caused by localized band-bending of the SWNT due to each Gd ion's field which is partially-screened by electrons in the encaging fullerene. Comparing images with different tip bias voltages, large DOS participating in the tunneling process, i.e. a large tip bias, might be needed to show enough spatial resolution. The scanning tunneling spectroscopy data of these nanotubes, which also show Gd-atom-induced local field-effect on the characteristic DOS features of SWNTs, will be presented. The possibility of 1-D Kondo effect due to the encapsulated Gd atoms will also be discussed.

9:00am **NT+EL+NS-ThM3 Using Carbon Nanotube Materials to Separate Molecular Mixtures: Predictions from Molecular Dynamics Simulations***,* ***S.B. Sinnott,*** The University of Florida*; Z. Mao,* The University of Kentucky*; K.-H. Lee,* The University of Florida*; R. Andrews, E.A. Grulke,* The University of Kentucky

Carbon nanotubes have been proposed as good materials for separation membranes because of their hollow, cylindrical shape and growth in ordered, close-packed bundles. We have therefore studied the manner in which molecular mixtures separate after diffusion into individual carbon nanotubes or nanotube bundles. The mixed systems considered in our study are methane/n-butane, methane/isobutane, methane/ethane, nitrogen/oxygen, nitrogen/carbon dioxide and oxygen/carbon dioxide. The computational approach used is classical molecular dynamics simulations where the forces on the atoms are calculated using empirical potentials that vary with distance.@footnote 1@ Short-range interactions are calculated using a many-body, reactive empirical bond-order hydrocarbon potential and the long-range interactions are characterized with Lennard-Jones potentials. Some of these molecular mixtures separate within individual nanotubes while others do not. The mechanisms by which the molecules diffuse through the nanotubes are found to play an important role in the separation of some mixtures. Molecular structure also has a large effect on the separation of the molecular mixtures. The helical structure of the nanotube walls is predicted to have no effect on results while the nanotube diameter has a large effect. As the diameter of the nanotubes increases, the amount of separation between the molecules decreases. In nanotube bundles, the diffusion behavior and coefficients of binary molecular systems change relative to the diffusion behavior in individual nanotubes. This research is sponsored by the NASA Ames Research Center and the Advanced Carbon Materials Center through the NSF (DMR-9809686). @FootnoteText@ @footnote 1@S.B. Sinnott, L. Qi, O.A. Shenderova, D.W. Molecular Dynamics of Clusters, Surfaces, Liquids, and Interfaces, Ed. W. Hase (JAI Press, Inc., Stamford, CT, 1999, pp. 1-26.

9:20am **NT+EL+NS-ThM4 Chemical Disentanglement of Single-Walled Carbon Nanotube Bundles***, N. Choi,* Joint Research Center for Atom Technology (JRCAT), Japan*;* ***H. Tokumoto,*** National Institute of Advanced Industrial Science and Technology (AIST), Japan*; Y. Maeda, T. Wakahara,* Niigata Univ., Japan*; T. Akasaka,* Univ. of Tsukuba, Japan*; H. Kataura, M. Kimura, S. Suzuki, Y. Achiba,* Tokyo Metropolitan Univ., Japan

Carbon nanotubes (CNTs) exhibit unique electronic and mechanical properties and chemical stability that cannot be realized in other materials, and therefore can be an important material in nanotechnology. Many applications have been demonstrated in the fi elds of materials science and technology, molecular electronic devices, and reliable probe tips for scanning probe microscopy. However, as-grown CNTs contain various contaminants such as catalysts and amorphous carbons, and have various lengths from a fe w nano-meters to milli-meters, and various sizes of bundles. These prevent us to use CNTs for various applications. Then, we have to develop several important key techniques such as how to purify, how to control length, how to disentangle the bundles, and how to disperse individuals in solvents. An important and essential technique to realize these keys is believed to be the chemical modification of CNTs combined with their sonication and centrifugation. In this paper, we will show the chemical process an d their characterization techniques. After purifying single-walled CNTs, we put them into N,N-dimethylformamide (DMF) at a concentration of 0.4 mg/10 ml with the small amount of amine. At the same time, we sonicated and centrifuged them under optimized ti m e, frequency and rotational speed. At each step, we measured a transmission electron microscopy (TEM), a Raman scattering spectroscopy, and an atomic force microscopy (AFM). These three techniques have proved that our technique has indeed worked out properly. Especially, the chemical modification of the CNT ends was confirmed by the AFM observation of CNTs covalently attached to gold colloidal particles.

9:40am **NT+EL+NS-ThM5 Electromechanical Properties of Carbon and Boron-Nitride Nanotubes***,* ***A. Zettl,*** University of California, Berkeley **INVITED**

The electronic properties of single- and multi-walled carbon nanotubes have been investigated via transport measurements under controlled environmental conditions, and in-situ electro-mechanical measurements inside a high resolution transmission electron microscope (TEM) and scanning tunneling microscope (STM). Our transport measurements show that the electronic structure of nanotubes is exceedingly sensitive to adsorbed gases. For example, the thermoelectric power for pure vacuum annealed tubes is negative, while that for oxygen-dosed samples is positive. Similarly, the electrical resistivity for individual tubes is sensitive to chemical environment, and nanotubes form robust oxygen and other chemical sensors. The theoretical basis for these sensitivities are explored via quantum transport models. For electromechanical studies, a special nanotube manipulator has been constructed for insertion into a TEM. Individual multi-walled nanotubes have been variously manipulated. We have discovered ways to peel and sharpen individual nanotubes (much like the sharpening process of a china marker pencil), pull the central core tubes out from (and reinsert them into) the outer nanotube shells of multi-walled tubes (nanotube "telescoping"), and induce nanotube collapse of cylindrical tubes into nanotube ribbons. Similarly, boron nitride nanotubes have been synthesized and the electromechanical response characterized in bulk and individually inside the TEM.

10:20am **NT+EL+NS-ThM7 Magnetic "Smart-Wires": Magnetic and Electronic Properties of Nickel and Iron Nanotubes Grown on Polypeptide Templates***, H. Matsui, S. Pan, E. Goun, M. Klimov,* ***B.P. Tonner,*** University of Central Florida

We describe a new architecture for spin-tronic magnetic devices, using a biologically modified, metal coated, peptide nanotube process which results in tubular, magnetic nanowires.@footnote 1,2@ The magnetic nano-wires are formed from a polypeptide backbone, coated with nickel, or iron, or with multilayers. The morphology of the tubes is that of a hollow, cylindrical metal pipe, with widths from 20-500nm, and lengths of up to a few microns. By functionalizing the ends of the tubes with special molecules, the nano-tubes can be "wired" to specific attachment sites on a substrate by molecular recognition. We call this a "smart-wire" concept, since the instructions for "wiring" the circuits are built into the molecular nanostructures themselves. In this paper, we describe magnetic and electronic transport measurements on aligned Nickel nanotube arrays and individual nanotubes, using both conventional and scanned-probe techniques. @FootnoteText@ @footnote 1@ Matsui, H.; Gologan, B., J. Phys. Chem. B. 2000, 104, 3383. @footnote 2@ Matsui, H.; Pan, S.; Gologan, B.; Jonas, S., J. Phys. Chem. B. 2000, 104, 9576.

10:40am **NT+EL+NS-ThM8 Chemical Reactivity of Carbon Nanotubes and Fullerenes***,* ***S. Park,*** Stanford University*; D. Srivastava,* NASA Ames Research Center*; K. Cho,* Stanford University

In most applications of carbon nanotubes and fullerenes, molecules are attached to either external or internal surface of carbon nanotubes and fullerenes to functionalize them. Therefore, the chemical reactions on nanotubes or fullerenes play an important role in understanding how to functionalize nanotubes and fullerenes. We have analyzed and compared the chemical reactivity of both external and internal surfaces of carbon nanotubes and fullerenes. The chemical reactivity analysis can be used to control the localized functionalization process as well as to predict energies and configurations of chemical reactions. Also this analysis can be applied to examine the storage capacity of carbon nanotubes and fullerenes. The chemical reactivity of carbon nanotubes and fullerenes can be characterized by a pyramidal angle, which is defined as the angle between @sigma@ bond and @pi@ orbital minus 90 degree. We analyze the chemical reactivity in terms of pyramidal angle. All analyses have been done by total energy density functional theory pseudo-potential method, and we have used a hydrogen atom as a point probe to investigate the chemical reactivity. We have developed a way to express the chemical relativity as function of pyramidal angle. We have found that the external chemical reactivity depends strongly on the initial pyramidal angle but the internal chemical reactivity is less sensitive to it. And we have also found that the internal chemical reactivity has more complex behavior than external chemical reactivity.

11:00am **NT+EL+NS-ThM9 Atomic Resolution Imaging of WS2 Nanotubes***, L. Scheffer,* ***S.R. Cohen,*** *R. Rosentsveig, R. Popovitz-Biro, R. Tenne,* Weizmann Institute of Science, Israel

Recent improvements in synthetic yields of inorganic nanotubes of metal dichalcogenides have enhanced the possibility of their technological applications.@footnote 1@ The unique optical and wear characteristics of these nanotubes make them ideal candidates for electromechanical systems.@footnote 2@ Correlation of the structural and electro-optical properties is a first step in this direction. Theory predicts delicate interplay between size, structure, and electrical properties of these nanotubes.@footnote 3@ Until now, correlation of the nanotube chirality with electrical properties has been indirect and scarce. In this work we present high resolution transmission electron microscopy (TEM) and atomic-resolution scanning tunneling microscopy (STM) images of nanotubes of WS@sub 2@. By relating the atomic registery to the tube-axis direction, the chirality of the tubes is determined. Current-voltage (I/V) spectroscopy in the STM was then applied to individual nanotubes to examine correlation between bandgap, density of states, and the nanotube chirality and size. @FootnoteText@ @footnote 1@ A. Rothschild, G.L. Frey, M. Homyonfer, R. Tenne, M. Rappaport, Mat. Res. Innovat. 3, 145 (1999). @footnote 2@ L. Rapoport, Y. Feldman, M. Homyonfer, H. Cohen, J. Sloan, J.L. Hutchison, and R. Tenne, Wear 229, 975 (1999). @footnote 3@G Siefert, H. Terrones, M. Terrones, G. Jungnickel, T. Frauenheim, Phys. Rev. Lett. 85, 146 (2000).

11:20am **NT+EL+NS-ThM10 In-situ Observed Atomic Structures at Carbon Nanotube Tips under Applied Electric Field*, T. Kuzumaki*,** *Y. Horiike,* The University of Tokyo, Japan*; T. Kizuka,* Nagoya University, Japan*; T. kona, C. Oshima,* Waseda University, Japan

Carbon nanotubes show characteristics that are of particular interest as electron sources for field emission displays. In this study, tip structures of the nanotubes were in-situ observed under applied electric field by using a high-resolution transmission electron microscopy (HRTEM), field ion microscopy (FIM) and also field emission microscopy (FEM). HRTEM used in this experiment equipped with newly designed two specimen holders system. HRTEM observation successfully revealed that the tip of the nanotube bent during the field emission and protrudent structure was formed along the normal to the electric field. The results demonstrate that the electric field exerted mechanical stress on the surface structure. The in-situ observations lead us to development of nano-processing technology of the nanotubes. We found that burst and evaporation, and bonding of individual nanotube tips can be performed by the contact with another nanotube, amorphous carbon, or metals at the applied voltage. The tip of the nanotube was burst and evaporated at the contact at the applied voltage of more than 2V. At the burst tip, each carbon layer was often connected with the neighbor layers. After the tip burst, however, two nanotubes were bonded at the contact when the applied voltage was less than 2V. A rod specimen in which the nanotubes are sticking out of the tip was fixed on the tungsten wire with carbon binder, and was introduced into the ultra-high vacuum chamber of 3X10@super-8@ Pa for FIM and FEM experiments. Prior to the FEM observation, we evaluated the cap structure of the nanotubes by FIM and confirmed that several bright areas as emission sites, and they were either deformed honeycomb structures composed of hexagonal or pentagonal carbon rings. The bright area sites of the honeycomb structures observed in FIM moved with increment of the applied voltage.

11:40am **NT+EL+NS-ThM11 Characterization of CVD Grown Carbon Nanotubes and Field Emission Properties*, C. Dong*,** *M. Gupta,* Old Dominion University*; G.R. Myneni,* Jefferson Lab, US

Carbon nanotubes(CNT) were synthesized by the thermal chemical vapor deposition with the decomposition of acetylene gas in the argon carrier gas under temperature of 700 ºC on Ni or hastelloy substrates. Carbon nanotubes were characterized by X-ray photoelectron spectroscopy (XPS), Raman Scattering, Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM). Field emission properties of well characterized carbon nanotubes was extensively studied. Low turn-on electric field of ~ 1V/um was achieved. Long-term stability of emission was studied. Field emission profile was examined by imaging using phosphor screen. Carbon nanotubes appear to have better field emission properties and stability comparing to Spindt type emitters.

Organic Films and Devices
Room 131 - Session OF+TF-ThM

Characterization of Organic Thin Films

Moderator: N.V. Richardson, University of St Andrews

8:20am **OF+TF-ThM1 Characterization and Modification of ITO Surfaces: Use of Chemisorbed Probe Molecules as Indicators of Electron Transfer Rates and Their Use in Improving OLED Performance*, C. Carter*,** *C.L. Donley, N.R. Armstrong,* University of Arizona

XPS characterization of ITO surfaces, following various pretreatments, shows that the surface coverage of hydroxyl groups, and oxygen defects, can be varied significantly. Probe molecules, such as ferrocene dicaroboxylic acid (Fc(COOH)2) can be chemisorbed to these surfaces through hydrogen bonding interactions, at coverages up to 40% of a compact monolayer. The coverage and electron transfer rates of these chemisorbed molecules vary by up to 100% depending upon pretreatments used. Organic light emitting diodes, prepared by spin coating single polymer layers (PVK), doped with Alq3, and its tri-sulfonamide analog, Al(qs)3, show signficant lowering of onset potentials for electroluminescence for ITO films modified with the Fc(COOH)2 probe, following air plasma cleaning. These differences in onset potential are most significant for devices where electron injection is not the chief limitation to electroluminescence.

8:40am **OF+TF-ThM2 XPS Characterization of Photo-Alignment of Liquid Crystals using Adsorbed Dichroic Materials*, L. Su*,** *J.L. West,* Kent State University*; Y. Reznikov,* Ukraine Academy of Science*; K. Artyushkova, J.E. Fulghum,* Kent State University

The alignment layer is one of the most important parts of a twisted nematic (TN) display. Many methods exist for producing alignment, and the quality of the alignment layer directly influences the performance of the display. The most popular alignment method used by the Liquid crystal display (LCD) industry is mechanical rubbing of a polymer film. However, there are many disadvantages associated with this method, such as the introduction of dust particles, formation of electrostatic charges and other defects on the rubbed surface. Photo-alignment of liquid crystals is emerging as one of the most promising substitutes for mechanical rubbing. Photo-alignment generates surface anisotropy through the interaction between the irradiated substrate and the light source. Photo-alignment using adsorbed dichroic materials provides an efficient and versatile way to produce effective alignment of liquid crystals. Successful photo-alignment results from properly matching the adsorbed and substrate materials. In this study, poly(vinyl) alcohol (PVA) and adsorbed dichroic materials, including the dye Brilliant Yellow, are utilized as the alignment layer. We will demonstrate the use of polarized UV-Vis spectroscopy and angle-resolved x-ray photoelectron spectroscopy (XPS) for studying the interaction of the polymer, dye and liquid crystal. Using ARXPS, it is possible to study the distribution of all three organic layers. Both techniques indicate that intermolecular interaction between the adsorbed dichroic molecules and the substrate polymer is critical to the outcome of photoalignment. This work has been supported in part by NSF ALCOM (DMR 89-20147), and the Air Force (DAGSI SN-AFIT-9903).

9:00am **OF+TF-ThM3 An STM , XPS and RAIRS Study of Cobalt(II) Hexadecafluorophthalocyanine (CoF16Pc) and Its Co-adsorption with Nickel(II) Tetraphenylporphyrin (NiTPP)on Au (111)*, S.L Scudiero*,** Washington State University, US*; D.E. Barlow, K.W. Hipps,* Washington State University

Scanning tunneling microscopy (STM) images show that cobalt(II) hexadecafluorophthalocyanine (CoF16Pc) forms disordered structures when deposited on Au(111) under UHV conditions at 300K, while nickel(II) tetraphenylporphyrin (NiTPP) forms a tightly packed well organized structure under the same conditions. X-ray photoelectron (XPS) and reflection-absorption infrared spectroscopy (RAIRS) data obtained on thin films of the pure compounds confirm that the chemical composition of these films is the same as the starting bulk materials. When CoF16Pc and NiTPP are co-deposited with a monolayer coverage, the resulting surface structure is a well ordered 2D array having a 1:1 ratio and a nearly square unit cell as revealed by high resolution STM images. The composition of the mixture was confirmed by XPS. We believe that this new structure is due to the weak electrostatic interactions associated with the local partial charges and their images, along with differences in Van der Waals forces.

9:20am **OF+TF-ThM4 Solution-Assisted Tribological Modification of Surfaces Using an Atomic Force Microscope*, F. Stevens,*** Washington State University, USAS*; R. Leach, J.T. Dickinson,* Washington State University

The response of thin polymer films to combined stress and solvent is important for applications such as protective barriers (e.g., various wrappings), in controlled drug release from polymer hemispheres, resists for lithography, and nanometer scale surface modification. Over a wide range of normal forces, when a polymer is scanned by SFM in contact mode in a solvent, material is not worn away, but rather the polymer surface expands forming a nanometer scale "bump" at and surrounding the scanned location. Furthermore, for sub-micron scan areas one often observes a series of parallel ridges (moguls) perpendicular to the fast scan direction. Previous reports of the formation of raised material have nearly all been in air, required long times or very high forces to form; little evidence has been presented for the mechanism of formation. We have engaged in a detailed study of protrusion formation and raised ridges using poly(methyl methacrylate) in alcohol based solvents. In addition to scanning in air, we have scanned the polymer surface in four solvents with dramatic differences in response. We have also observed the effects of varying contact force, and the effect of using cantilevers with different force constants. We present evidence that both plastic deformation and tip induced swelling play major roles in the observed polymer surface modification by SFM. The stresses applied by the tip generate tensile forces around the tip that likely increase the quantity of solvent that can enter the surface. We show that adding Rhodamine 6G dye to the solvent provides us with evidence that indeed solvent is going into the polymer. Using fluorescence microscopy we can monitor the uptake of dye as a function of scanning and solvent parameters. This study also shows the possibility of introducing small quantities of a chemical into the polymer surface in a highly localized (nanometer scale) fashion.

9:40am **OF+TF-ThM5 Viscoelastic Properties of Thin Liquid Crystal Films*, I. Zori@aa c@*,** *P. Borchard, T. Carlsson, B. Kasemo,* Chalmers University of Technology, Sweden

Viscoelastic properties of thin liquid crystal (LC) films are strongly affected by the changes in orientational and/or translational order in the system. These changes may be induced via a temperature variation or by a presence of the two phase interface (e.g. a free surface or a LC-solid substrate interface). In this contribution we report the viscoelastic properties of thin (500-7000Å) 5CB films, spin coated on the Au electrode of the quartz crystal microbalance (QCM), with one free surface. The system (LC film) is exposed to a periodic shear force (at 5 MHz respectively 15MHz) and the changes in the QCM oscillator frequency, @DELTA@f, and dissipation factor, @DELTA@D, are measured as a function of temperature while the system undergoes a series of phase transitions (smectic-nematic-isotropic). Both @DELTA@f and @DELTA@D show unusual temperature dependence in the vicinity of the nematic-isotropic phase transition. Two approaches are used to deduce the temperature dependent viscoelastic coefficients from the measured frequency and dissipation factor changes. In both approaches the QCM is treated as a harmonic oscillator and the Navier Stokes equation is used to calculate the velocity profile in the viscous overlayer caused by the periodic shear. Once the velocity profile in the film is known, a frictional force causing a change in the oscillator frequency and dissipation, may be calculated. In the first case the overlayer is treated as a homogenous isotropic thin liquid film (Voight model) while in the second case a proper anisotropic structure of the LC film is taken into account in the hydrodynamic continuum approach (Leslie-Ericksen theory). We compare our results to generalized viscosities obtained using different methods.

10:00am **OF+TF-ThM6 Structure of Ultrathin Pentacene Films*, S. Lukas*,** *G. Witte, C. Wöll,* Ruhr-Universität Bochum, Germany

The structure of ultrathin films (1-3ML) of pentacene grown by evaporation under UHV conditions on various copper surfaces has been studied by LEED, STM and NEXAFS. The enhanced binding energy of acene molecules at step edges which was measured systematically by TDS can be utilized to prepare ordered monolayer films on vicinal copper surfaces with close packed terraces while only disordered films grow on the flat Cu(111) surface.@footnote 1@ Highly ordered mono- and multilayer films were also obtained for the Cu(110) surface and their corresponding molecular orientation was determined by NEXAFS as a function of the film thickness. For comparison additional films were grown also on gold and sapphire surfaces. In addition to the geometrical structure the electronical properties of these pentacene films were investigated by UPS. @FootnoteText@ @footnote 1@ S. Lukas et al., J. Chem. Phys. 114 (2001) .

10:40am **OF+TF-ThM8 Photoelectron Spectroscopy of Exciton Dynamics and Interactions in Organic Thin Films: C@sub60@ and Photopolymerized C@sub60@*, J.P. Long*,** *S.J. Chase, M.N. Kabler,* Naval Research Laboratory

Of fundamental importance to the operation of many organic electronic devices are the controlling nonequilbrium populations of singlet (S@sub 1@) and triplet (T@sub 1@) excitons and charged carriers. For example, optoelectronic device efficiencies may be depressed if dark T@sub 1@ excitons compete with fluorescent S@sub 1@ states or if annihilation interactions limit excited state population densities. Because pump-probe photoelectron spectroscopy is uniquely capable, in principle, of resolving in energy and time the electrons of all nonequilibrium species, it promises to provide useful insights into the densities, lifetimes, and mutual interactions of the various nonequilibrium populations. Using both synchrotron and laser-harmonic photoemission sources, we have applied this technique to study the dynamics of excitons pumped by visible laser radiation in the model systems of C@sub 60@ and photopolymerized C@sub60@ films prepared in ultrahigh vacuum and studied in situ. We report the unambiguous identification of the transient photoelectron spectra of both S@sub 1@ and T@sub 1@ excitons. Studies on time scales from 100 ps to 10 µs and of exciton concentrations from below 10@super 18@ cm@super -3@ to more than 10@super 19@ cm@super -3@ reveal a rich dynamics. For exciton densities above ~10@super 19@ cm@super -3@, excited-state interactions lead to a surprising excess of T@sub 1@ excitons at the expense of S@sub 1@ excitons for times much less than the intersystem crossing time of ~2.5 ns. Such excess T@sub 1@ generation suggests that interactions among excited species may interfere with the operation of potential devices that would operate at high nonequilibrium densities. A rate-equation model that couples interacting S@sub 1@, T@sub 1@, and carrier populations reproduces the complex dynamics, including non-Markovian decays, and provides evidence for the annihilation of excitons by charged carriers.

11:00am **OF+TF-ThM9 Optical Properties of Highly Ordered Ultrathin Epitaxial Films of PTCDA on Au(111)**, *R. Nitsche, S. Mannsfeld, H. Proehl,* ***T. Fritz,*** TU Dresden, Institut fuer Angewandte Photophysik, Germany

Highly ordered organic thin films on a gold single crystal have been prepared by means of organic molecular beam epitaxy and investigated by optical absorption spectroscopy. The organic dye molecule perylene-3,4,9,10- tetracarboxylic-3,4,9,10-dianhydride (PTCDA) has been deposited on Au(111) with submonolayer to multilayer coverage. All films were structurally characterized by combining Scanning Tunneling Microscopy (STM) with Low Energy Electron Diffraction (LEED), clearly indicating epitaxial growth in the point-on-line mode. In order to determine the optical constants of those films, Differential Reflection Spectroscopy (DRS) has been applied. Subsequently, the optical constants have been calculated based on a model dispersion formula, thereby deconvoluting the absorption index k into several molecular transitions. The thickness dependence of the parameters (position, width, strength) of those transitions is discussed. Contrary to a simple discussion of the peak position of the entire spectrum, which would indicate an energetic shift, our thorough analysis reveals that the dominant effect consists of a change in the relative contributions of the several transitions rather than an energetic shift. The results are compared to polycrystalline PTCDA layers of comparable thickness on polycrystalline gold films, exhibiting a larger inhomogeneous broadening.

11:20am **OF+TF-ThM10 Importance of Structural Order for the Low Surface Energy of Perfluoroalkyl Substituted Polymethacrylates*, J. Luning*,** Stanford University*; D.Y. Yoon,* Seoul National University, Korea*; J. Stohr,* Stanford University

Perfluoroalkyl substituted PolyMethacrylate (PFPM) polymers are today widely used as low surface-energy coatings playing an essential role in microelectronics, anti-fogging, and anti-fouling applications, and even have promising medical applications. It is generally believed that the anti-wetting properties -solely determined by the structures present in the surface region- of these and related polymers arise from the segregation of CF@sub 3@ groups to the surface. However, proof of a direct correlation between surface structure and surface energy, and the importance of order in the underlying bulk, is still lacking as most experimental techniques do not have the required surface sensitivity. For preferentially oriented polymers the asymmetry in chain orientation translates to an asymmetry in the electron charge density as the electron orbitals are oriented along the molecular bonds. Such a charge asymmetry can give rise to a dependence of the Near Edge X-ray Absorption Fine Structure (NEXAFS) on the orientation of the electric field vector of the linearly polarized x-rays relative to the sample. Consequently, such a linear dichroism can be used to study orientation phenomena quantitatively. The required surface sensitivity is obtained by recording simultaneously the more bulk sensitive total (TEY) and the more surface sensitive Auger (AEY) electron yield. Our studies of three PFPM's with different bulk order phases reveal a greater order at the surface than in the bulk, and the surface order parameter is found to correlate with the surface energy. Most importantly, temperature dependent NEXAFS measurements covering several bulk phase transitions show that the achievable surface order, and hence the surface properties, is ultimately limited by the bulk order (phase).

Photonics Materials Topical Conference
Room 120 - Session PH-ThM

Photonic Materials: Studies on the Nano Scale

Moderator: K. H. A. Bogart, Bell Laboratories, Lucent Technologies

8:20am **PH-ThM1 Chalcogenide Glasses as Nonlinear Optical Materials and Their Application in Optical Communication Systems***, **H.Y. Hwang,*** Bell Laboratories, Lucent Technologies **INVITED**

Chalcogenide glasses exhibit an enhanced Kerr nonlinear refractive index n2, which can be used in a number of applications such as optical switching, pulse shaping, etc. We have explored a range of bulk chalcogenide glasses for optimization at communications wavelengths (~1.55 ?m), motivating current experiments in thin film planar waveguides as well as fiber devices. Low-loss single mode waveguides have been fabricated in a number of ways, and their linear and nonlinear optical properties will be presented. Strong Bragg gratings have also been fabricated using replica molding from holographically generated templates. Finally, the use of chalcogenide films as lateral waveguide cladding of semiconductor optical devices will be described.

9:00am **PH-ThM3 Crystallization Kinetics in Chalcogenide Glasses***, **S. Ziegler,*** Aachen University Technology, Germany, Aachen

Chalcogenide alloys are frequently used for rewritable optical data storage where submicron sized regions of the film are switched between an amorphous and a crystalline state. Since the kinetics of this process are crucial for the success of the technology employ a combintion of different techniques to study the transformation. The activation energy for crystallization is determined by measurements of the electrical resistance upon heating. The structural changes upon heating is derived from x-ray diffraction while x-ray reflectometry is employed to measure the density change upon crystallization. For a number of different alloys density and thickness changes upon crystallization between 5 and 10% are observed. These density changes are accompanied by irreversible stress changes which could possibly limit the lifetime of the films. Nevertheless the measured stress change is much smaller than the stress change expected for a purely elastic deformation. This can be explained by a viscous flow of the amorphous pulse which can also account for the changes of film topography upon crystallization is observed by atomic force microscopy. Microscopic measurements of the crystallization kinetics reveal of correlation with the film stoichiometry, in particular the relative abundance of Ge-Te bonds in GeSbTe alloys. Concepts of combinatorial synthesis are employed to identify phase change materials with fast transformation kinetics.

9:20am **PH-ThM4 Single Quantum Dots as Tunable Artificial Atoms***, **D. Hessman,** M. Holm, J. Persson, M.-E. Pistol, C. Pryor, L. Samuelson,* Lund University, Sweden **INVITED**

We present micro-photoluminescence studies of self-assembled InP quantum dots (QDs) embedded in GaInP. The QDs are pyramid shaped and usually about 15 nm high, with a slightly elongated base of about 40 by 50 nm. There are however also smaller QDs with similar lateral extension but with a considerably smaller height. The change in size is, as expected, accompanied by a change in quantum confinement with a corresponding change in emission energy. In addition, there is a transition from a single sharp emission peak for the smallest dots to several 1 meV broad emission lines emitted over a 50 meV energy range for the largest dots. The reason for this behaviour is unintentional doping in the barrier material, resulting in electron accumulation in the QDs. This gives rise to emission in an energy range corresponding to the energy range occupied by these electrons. Larger QDs accumulate more electrons and thus emit over a larger energy range. For the largest dots, the number of electrons is large enough that Coulomb-induced dephasing sets in, resulting in a dramatic line-width broadening. By depositing a semi-transparent Schottky gate on top of the sample, photoluminescence spectra of single QDs can be obtained as a function of bias. Varying the bias, the number of electrons in a large QD is tuned in the range 0-15. For biases such that only a few electrons are present in the QD, the Coulomb-induced dephasing is reduced and the originally 1 meV broad lines split up into sharp lines. We conclude that InP/GaInP is a very interesting system, with QDs acting as tunable artificial atoms, controllable both by size and external bias.

10:20am **PH-ThM7 Dynamic Response of the Electro-optic Effect in Epitaxial Ferroelectric Thin Films***, **B.W. Wessels,*** Northwestern University **INVITED**

Ferroelectric thin films are of considerable promise for use as electro-optic, and non-linear optical materials. Electro-optic (EO) waveguide devices fabricated from thin films offer several advantages over bulk material including lower driving voltages, smaller size, higher modulation speeds and the potential for monolithic integration. Recently we reported ferroelectric thin film electro-optic modulators that operate at frequencies up to 20 GHz. We have also investigated the dynamic response of the electro-optic effect in thin film BaTiO@sub 3@ and KNbO@sub 3@ . The dynamic response has a temporal dependence given by the expression t@super -m@exp(-Bt)@super n@. Measurements of the film birefringence, polarization and dielectric transients show qualitative agreement over 11 orders of magnitude in time. The observed dependence is attributed to the dynamic response of ferroelectric domains.

11:00am **PH-ThM9 Two-stage Growth of Patterned Epitaxial Lithium Niobate for Photonic Application***, V. Joshkin,* University of Wisconsin-Madison*; K. Dovidenko, S. Oktyabrsky,* NYS Center for Advanced Thin Film Technoogy*; D. Saulys, T.F. Kuech,* ***L. McCaughan,*** University of Wisconsin-Madison

LiNbO3 is an ideal material for linear and nonlinear photonic crystals. Potential commercial applications have long been frustrated by the chemical stability of this material. We present a new two-stage growth method for fabricating patterned crystalline LiNbO3 structures for photonic applications. The method is based on physical and chemical properties of amorphous and polycrystal LiNbO3 films grown by high pressure chemical vapor deposition (CVD) from metal alkoxide precursors. In the first stage, the CVD technique is used to deposit amorphous or polycrystalline LiNbO3 films on a crystalline substrate at high deposition rates (~2micron/hr). Patterned structure can now be formed after this first stage using a rapid wet or dry etching of amorphous LiNbO3 (up to 6micron/min depending on etching regimes). In the second stage, a post-growth anneal at high temperature(900°C- 1100°C) converts the film to single crystal LiNbO3. Under the proper annealing conditions, the LiNbO3 bulk self-diffusivity dominates the surface mobility, allowing epitaxial films that maintain the shape of micron-size pattern. These patterned structures are characterized by AES, SEM, HRTEM and DXRD. The effect of substrate on film quality is investigated. Lift-off processing on films grown by two-stage growth technique is demonstrated. Comparison of high vacuum chemical beam epitaxy with high pressure CVD from alkoxides is performed.

Plasma Science
Room 104 - Session PS+MS-ThM

Conductor Etch and Damage

Moderator: A.E. Wendt, University of Wisconsin, Madison

8:20am **PS+MS-ThM1 An Advanced 300 mm Etcher with Tunable Plasma Source for the Etching of <0.15mm Poly-Silicon Gates***, **J. Holland,*** Applied Materials, Inc., US*; M. Jain, M. Shen, N. Gani, A.M. Paterson, V. Todorov, M.S. Barnes, K. Fairbairn,* Applied Materials, Inc.

The current requirements for etch performance for 300mm poly-silicon gate can only be met by providing a wide enough process window that is capable of achieving uniform etching for the variety of steps needed to complete this etch. The final dimensions of the polysilicon gate are functions of the many different etch steps, the ARC/DARC open, the main-etch , soft landing step and over-etch steps. In order to achieve < 10 nm CD range for <0.15 um polysilicon features, all of these steps need to be very uniform and the CD loss (or gain) needs to be very controllable. In this next generation 300 mm etcher, a tunable inductively coupled plasma source combined with advanced gas injection technology allows etch uniformity to be optimized for all of these different steps. Results of tuning for etch uniformity will be shown. CD control of <5 nm with a total range of 10 nm is achieved. The tunable source is also combined with a precise wafer temperature control using a dual-zone electrostatic chuck to ensure CD uniformity can be achieved across the entire diameter of the 300mm wafer. The wide process window of this etcher should be capable of addressing both current and evolving applications which require etching of multiple films with multiple etch steps involving varied process conditions.

8:40am **PS+MS-ThM2 Plasma-Based Copper Etch Process - Additive Gas Effects***, **S. Lee**[1], Y. Kuo,* Texas A&M University

Copper is an ideal multilevel interconnection material for VLSIC and many other microelectronic devices. However, it is difficult to etch copper into fine lines by the conventional plasma etching method under a mild process condition such as at room temperature or without the inclusion of an extra energy source, e.g., UV, IR, or a high-density plasma source. Recently, authors reported a new plasma-based copper etching method that showed a high etch rate at room temperature using a parallel-plate electrode design.@footnote 1,2@ The success of this method relies on a novel plasma-copper reaction. Instead of removing copper compounds during the plasma processing, copper was converted into a solution soluble compound accumulated on the surface. This reaction product was subsequently removed with a HCl solution. The resulting copper pattern has a vertical profile. In this paper, we are going to discuss the additive gas (Ar, N@sub 2@, CF@sub 4@, and O@sub 2@) effects on the Cl@sub 2@ plasma-based copper reaction process. In addition to the reaction rate, the product's morphology, structure, and the undercut of the photoresist pattern have been studied. The added gas can enhance or hinder the reaction rate and the progress in the radial direction through various mechanisms. Experimental results are interpreted by the plasma phase chemistry, ion bombardment phenomena, and the original copper structure. The composition and chemical states of the reaction product are characterized by EDS and XPS. The film's morphology and structure are examined by AFM, SEM, and XRD. This study enhances our understanding of the unique plasma-based copper etching process that is critical to many microelectronic and optoelectronic applications. Authors would like to acknowledge staffs in the CIMS of Texas A&M University for AFM and XPS analyses. @FootnoteText@ @footnote 1@ Y. Kuo and S. Lee, Appl. Phys. Lett. 78, 1002, (2001) @footnote 2@ Y. Kuo and S. Lee, Jpn. J. Appl. Phys. 39, L188, (2000).

9:00am **PS+MS-ThM3 Silicon Gate Etching: Potential Strategies for Future CMOS Devices***, **G. Cunge**, L. Vallier, O. Joubert, J. Foucher, X. Detter,* CNRS/LTM, France **INVITED**

In less than ten years CMOS devices will operate in the sub-50 nm gate length regime. The fabrication of the gate will be the key issue of the device fabrication process since the variation in gate dimension must not exceed the nominal CD targeted by few nm. In this work, some of the most promising gate strategies are investigated 1) resist mask on SiON antireflective layers versus hard mask approaches 2) standard HBr/Cl@sub2@/O@sub2@ chemistries versus CF@sub4@ (or NF@sub3@) added chemistries. The origin of CD deviation are investigated for each single step of the different strategies: correlations between chemistry and plasma operating conditions analysed by mass spectrometry, passivation layer formation on the feature sidewalls analysed by XPS and CD deviation will be established. Our preliminary experiments show that the passivation layers formed on the mask sidewalls induce very severe CD gain during standard gate etch steps. The objective is first to minimize the CD deviation induced by each individual step of the process (by decreasing the passivation layer thickness). Ultimately, the process has to be tuned so that the CD loss or gain of each individual step compensate each other to maintain the CD in the targeted window. In final, by comparing the impact of mask materials as well as the impact of chemistries (standard or clean) on CD control, we may give some interesting conclusions on the most promising strategy. In parallel to this study, we evaluate the current strategies used to obtain gates smaller than the dimension printed by the lithography (resist trimming or "notched gate approach") and try to draw some clear conclusions on the best approach for manufacturing.

9:40am **PS+MS-ThM5 Sidewall Passivation Mechanism of CF@sub4@ Added Polysilicon Gate Etch Process***, **T. Lill**, F. Ameri, S. Deshmukh, D. Podlesnik,* Applied Materials*; L. Vallier, O. Joubert,* CNRS/LTM, France

For the traditional HBr/Cl@sub2@/O@sub2@ gate etch process, anisotropy is achieved by forming silicon, oxygen, and halogen containing compounds on the sidewall of the etching structures. These compounds inhibit the isotropic etch and are removed by from the etch front via ion sputtering and ion assisted desorption. The introduction of fluorine via CF@sub4@ to a typical HBr/Cl@sub2@/O@sub2@ polysilicon etch process suppresses the formation of SiOxBry or SiOxCly via formation of volatile SiF@sub4@. Speculations that carbon based polymers play an important role in the sidewall mechanism for the CF@sub4@ polysilicon gate etch chemistry have recently been confirmed by in-situ XPS studies in the Silicon DPS chamber at CNRS/LETI in Grenoble. In this paper we present more detailed studies of the sidewall composition for different CF@sub4@ and O@sub2@ flows. The results suggest the coexistence of silicon oxyhalogenides and carbon polymers on the sidewall for theHBr/Cl@sub2@/CF@sub4@/O@sub2@ gas mixture. The carbon content in the sidewall passivation layer increases strongly when the oxygen flow is reduced. The XPS results will be correlated with findings on chamber wall condition (oxide or carbon mode), change of the critical dimension for dense and isolated lines during gate etching (critical dimension microloading), and etch rate differences between doped and undoped polysilicon. We will present experimental line width data that corroborate the idea of change in sidewall passivation from compounds that are formed on the etching surface (silicon oxyhalogenides) to compounds formed in the gas phase (carbon polymers) when CF@sub4@ is added to the plasma. Typically, profile and critical dimension microloading are significantly reduced for the CF@sub4@ added chemistry as a result of the change in the sidewall passivation mechanism. The superior etch performance and the increased productivity due to clean chamber walls explain the rapid acceptance of this polysilicon gate etch chemistry in high volume VLSI production.

10:00am **PS+MS-ThM6 Manufacturing Viability of the "Notched Gate" Process for sub 0.1µm Technologies***, **J. Foucher**[2], L. Vallier, G. Cunge, O. Joubert,* CNRS/LTM, France*; T. Lill,* Applied Materials

The development of new integrated circuit generations, at a unique rate in the semiconductor history, imposes the development of new technologies. Recently, Integrated Circuit manufacturers have evaluated new strategies to make gate transistors smaller than the resolution allowed by the lithographic tool available for manufacturing. One of them is to decrease the resist feature dimension before gate etching (resist trimming), the other approach is to design a "notched gate" etch process with a controlled etch rate of silicon in the lateral direction (the bottom of the gate is smaller than its top). We first describe in details the main differences between a notched gate process and a standard gate etch process and introduce the notion of passivation layer engineering. We demonstrate that when the process is accurately tuned, gate dimension of 10 nm can be obtained on a 200 mm diameter wafer. We mainly concentrate on several aspects of the process which determine its industrial viability: - What are the plasma operating conditions and chemistry required to stabilize a "notched gate" process or in other words what are the impact of the wall conditions on notch reproducibility ? - Can we solve the CD control issues of the notched gate process ? We will present experimental data demonstrating clearly that the notch depth rate is strongly dependent on the gate environment. In other words, the lateral etch rate which controls the notch depth is aspect ratio dependent and impacted by the plasma non-uniformity. In conclusion, we clearly demonstrate the strong limitations of the notched gate process for manufacturing.

10:20am **PS+MS-ThM7 Properties of Pulsed ICPs with rf Substrate Biases@footnote 1@***, P. Subramonium, **M.J. Kushner**,* University of Illinois

Pulsed inductively coupled plasmas (P-ICPs) are of interest for controlling reactive fluxes to the substrate in microelectronics fabrication. In particular, negative ion fluxes to the wafer can be obtained in electronegative pulsed plasmas. In order to achieve anisotropy of the fluxes, rf substrate biases must also be used with P-ICPs. This is problematic since the increase in plasma potential obtained with an rf bias tends to trap negative ions. A moderately parallel implementation of the 2-dimensional Hybrid Plasma Equipment Model (HPEM) was used to investigate P-ICPs in electronegative gas mixtures having continuous and pulsed rf substrate biases. Electron properties are obtained using a Monte Carlo Simulation. In Cl@sub 2@ at 10 mTorr (PRF=10 kHz, duty cycle 50%), the electron temperature, after falling in the first part of the afterglow, increases in the late afterglow signifying a transition to a capacitive mode. The onset of the increase in T@sub e@ comes earlier with increasing rf bias voltage. The increase can be attributed to progressively larger rates of sheath heating resulting from the decreasing electron density, increasing sheath width and increasing sheath speed. Coincident with the increase in T@sub e@ comes an increase in sheath potential which prevents negative ions from escaping from the plasma. @FootnoteText@ @footnote 1@Work supported by NSF, SRC and Applied Materials.

10:40am **PS+MS-ThM8 Magnetic Field Effects and Electron Shading Damage***, **W.W. Dostalik**,* Texas Instruments, Inc.

The use of magnetically enhanced plasma etch systems (MERIE) is widespread in semiconductor manufacturing. A primary concern with such

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[1] **PSTD Coburn-Winters Student Award Finalist**

[2] **PSTD Coburn-Winters Student Award Finalist**

systems is the risk of plasma process induced damage. In this paper, we discuss several of the candidate mechanisms in which magnetic fields may affect plasma damage associated with the electron shading effect (ESE). In particular, we consider for the case of a permanent magnet MERIE reactor the effects of guiding center drifts (e.g., gradient drift and curvature drift) on charged particle fluxes, of magnetic field effects on individual trajectories, and of non-uniformity in a typical magnetic field map. These effects are calculated in a two-step fashion. In the first step, an experimentally measured magnetic field map of a commercial plasma reactor is input into a computer program that calculates the various drift velocities and non-uniformity for typical plasma parameters. In the second step, the results of these calculations are used to affect incoming charged particle fluxes in local scale Monte Carlo simulations including the magnetic field and local topography. Charge accumulation and the resulting Fowler-Nordheim injection current are accounted for in the Monte Carlo simulations.

11:00am **PS+MS-ThM9 Effects of H@sub 2@, D@sub 2@, N@sub 2@ and Ar Plasma on III-V Compound Semiconductor Devices*, B. Luo,*** University of Florida*; K. Ip,* Agere Systems*; F. Ren, K.P. Lee, S.J. Pearton, C.R. Abernathy,* University of Florida*; R.J. Shul,* Sandia National Laboratories*; S.N.G. Chu,* Agere Systems*; C.W. Tu,* University of California, San Diego*; C.S. Wu,* Win Semiconductor*; K.D. Mackenzie,* Unaxis USA Inc.*; C.H. Hsu,* Feng Chia University, Taiwan

The effects of H@sub 2@, D@sub 2@, N@sub 2@ and Ar plasma exposures on the dc and rf characteristics of pseudomorphic AlGaAs/InGaAs high electron mobility transistors (HEMTs), GaAs metal semiconductor field effect transistors (MESFETs), and AlGaAs/GaAs heterojunction bipolar transistors (HBTs) were investigated. The experiments were conducted in a Plasma Therm 790 inductively coupled plasma (ICP) system. The influences of rf chuck power(10-100W), ICP source power(100-800W), chamber pressure(2-10mtorr) and durations(10-240sec) on device performance were studied. To analyze the rf results, a device equivalent circuit model was proposed to realize damage effects on the transistor small-signal elements. Several plasma damage mechanisms were identified for the degradations of device dc and rf characteristics, including creation of surface and bulk deep level recombination centers, preferential loss of As atom from the surface due to energetic ion bombardment and passivation of Si donors by formation of Si-H and Si-D neutral complexes. Auger and atomic force microscopy (AFM) were also used to characterize the atomic ratio and roughness of plasma damaged surface, respectively.

11:40am **PS+MS-ThM11 Plasma Induced Physical Damage and Contamination on the SrBi@sub 2@Ta@sub 2@O@sub 9@ Thin Film after Etching in Cl@sub 2@/CF@sub 4@/Ar Plasma*, D.P. Kim,*** *C.I. Kim,* Chung-Ang University, Korea*; W.J. Lee, B.G. Yu,* ETRI, Korea

SrBi@sub 2@Ta@sub 2@O@sub 9@ (SBT) have been developed as dielectric materials of capacitor. To fabricate high density FRAM, plasma etching is indispensable process for the anisotropic pattern definition because it has good selectivity and excellent process control. However, the detrimental impact of plasma etching process on device characteristics has been existed. As feature size decreases, the plasma induced damages can decrease the performance of device. The plasma induced damages can be broadly classified as residue contamination, plasma-caused species permeation, bonding disruption and current flow damage. Etching mechanism and damages on SBT thin film during etching process have less reported in the literature. SBT thin films were etched in Cl@sub 2@/CF@sub 4@/Ar plasmas with measuring etch rates at different etching parameters such as gas mixing ratio, rf power, dc bias voltage, and chamber pressure. The maximum etch rate was 1060 Å/min in Cl@sub 2@(10)/CF@sub 4@(20)/Ar(80). The small addition of Cl@sub 2@ into CF@sub 4@(20)/Ar(80) plasma will decrease the fluorine radicals and the increase Cl radical. The etch profile of SBT thin films in Cl@sub 2@/ CF@sub 4@/Ar plasma is over 80°. The chemical reactions on the etched surface were investigated with x-ray photoelectron spectroscopy (XPS). Atomic force microscopy (AFM) was used to investigate the surface morphology of SBT thin films exposed in plasma. High-resolution transmission electron microscopy (TEM), secondary ion mass spectrometry (SIMS) and x-ray diffraction (XRD) were evaluated in order to investigate physical damages. Electrical properties were characterized by measuring leakage current and hysteresys loop of Pt/SBT/Pt capacitor. From the results, damages in SBT etching was occurred in the near surface and Ar ion bombardment and nonvolatile etching by products caused to change of crystallinity and surface morphology.

Semiconductors
Room 111 - Session SC+SS+EL-ThM
Interaction of Hydrogen and Organics with Silicon

Moderator: C.B. Musgrave, Stanford University

8:20am **SC+SS+EL-ThM1 Prepairing-dependent Desorption Kinetics of Hydrogen from Si(100)-2x1*, H. Nakazawa,*** *M. Suemitsu,* Tohoku University, Japan

The reason why H@sub 2@ desorption from Si(100) surface shows a first-order desorption kinetics has been a controversial issue for more than a decade, and various desorption models have been proposed accordingly. Although most of the models assume prepairing of surface hydrogen atoms at a dimer as a precursor state, few attempts have ever been made to confirm its role in the desorption kinetics. We here show that the reaction order for the H@sub 2@ desorption from Si(100) can be varied by changing the hydrogenating gas and the thermal condition of the hydrogenation and that its behavior is systematically interpreted as a change of fractional coverage of paired hydrogen atoms. Three hydrogenating gases (atomic hydrogen (H), silane, and disilane) and three thermal conditions (room-temperature adsorption (RT), high-temperature adsorption (HT), and post-annealing (PA)) were tested. The desorption kinetics was analyzed by the peak position, the spectral shape, and their coverage dependence of the temperature-programmed desorption (TPD) spectra. As a result, the desorption kinetic order increased as H < disilane < silane and RT < HT < PA. To investigate the microscopic detail, we developed a set of rate equations for desorption with a fractional coverage of unpaired hydrogen atoms being chosen as a key parameter, which described the whole variation of the TPD spectra quantitatively. Using the obtained parameter, we argue the dependence on the hydrogenating gas in terms of different arrangements of surface H atoms. The dependence on the thermal condition is explained by a selective desorption from paired hydrogen atoms as well as the dissociation of paired hydrogen atoms during thermal treatments.

8:40am **SC+SS+EL-ThM2 In situ Measurements of the Stability of H terminated Si Surfaces and Kinetics of Oxide Regrowth in Ambient*, V. Fomenko*,** *D. Bodlaki, E. Borguet,* University of Pittsburgh

The passivation of semiconductor surfaces is key to the operation of semiconductor devices. HF treatment removes native and deposited oxides from silicon. The resulting H-terminated surface is technologically and fundamentally important, and has been subject of a number of experimental and theoretical studies. H termination on Si surfaces has been considered to a stable in air at least for semiconductor wafer processing time scales. However, there is some disagreement as to the timescale of stability. In part this depends on the experimental probes. Using SHG, ellipsometry,contact angle, STM and AFM we have investigated the stability of the surface in ambient and under laser irradiation. in-situ second harmonic generation (SHG) experiments probe the oxide regrowth on hydrogen terminated Si(111) surfaces via SHG rotational anisotropy that is sensitive to hydrogen termination via changes the nonlinear optical response of the interface, both in the magnitude and shape of the SHG rotational anisotropy patterns. In addition, laser induced oxidation of H passivated Si(111) surfaces can be induced with intense ultrashort near IR laser pulses.

9:00am **SC+SS+EL-ThM3 Hydrogen and Si(001): Adsorption/Desorption Pathways and the "Barrier Puzzle"*, F.M. Zimmermann,*** Rutgers University
INVITED

Although dissociative adsorption of molecular hydrogen on Si(100) is thermodynamically favored by an adsorption energy of almost 2 eV, the sticking probability is immeasurably small (less than 10@super -11@) at room temperature, indicating the presence of a large energy barrier to adsorption. An adsorption barrier is expected to manifest itself in desorption as well by imparting hyperthermal amounts of kinetic energy to the desorbing molecules. Surprisingly, however, H@sub 2@ molecules associatively desorbing from Si(001) show no signs in their translational or rotational kinetic energy distributions of having traversed such a barrier, in apparent contradiction with microscopic reversibility. We have obtained experimental and theoretical results resolving this long-standing puzzle. Using surface second harmonic generation as a sensitive coverage probe, we observed that the dissociative sticking probability increases markedly with hydrogen coverage, and decreases with exposure pressure. Both dependencies are very unusual and impose severe constraints on the adsorption mechanism. By combining detailed measurements of the adsorption and desorption kinetics with statistical mechanical modeling and ab initio calculations, we arrived at a quantitative, mechanistic description of adsorption/desorption consistent with all observations and providing a natural explanation of the barrier puzzle. The model involves two distinct reaction pathways. At intermediate to high hydrogen coverages, thermal adsorption and desorption are dominated by an adsorption-barrier free, autocatalytic pathway, while a non-autocatalytic, bare-dimer pathway with a ~0.7 eV adsorption barrier dominates at very low coverages. Fitted model parameters are in quantitative agreement with density functional theory calculations.

9:40am **SC+SS+EL-ThM5 Noncontact AFM Study for Hydrogen Termination on Silicon Surfaces***, **Y. Sugawara**, S. Morita,* Osaka University, Japan **INVITED**

In order to most effectively apply the noncontact atomic force microscopy (AFM) using frequency modulation (FM) technique as a science tool in a variety of fields such as surface science, it is very important to understand fully the imaging mechanisms of the noncontact AFM on various samples. The imaging mechanism has been investigated on a chemically reactive surface such as semiconductor surface and an insensitive surface such as pure metal surface and layered material surface. However, there is no report of a comparative study between a reactive surface and an insensitive surface using same tip. For instance, Si(100)2x1:H monohydride surface is that a Si(100)2x1 reconstructed surface is terminated by a hydrogen atom, and do not newly reconstruct as metal deposited semiconductor surface, and the surface structure hardly change. Thus, Si(100)2x1:H monohydride surface is one of most useful surface for a model system to investigate the imaging mechanism, experimentally and theoretically. However, there is no report for noncontact AFM imaging on Si(100)2x1:H monohydride surface, and whether the interaction between a very small atom as hydrogen and a tip apex is observable with noncontact AFM do not have been clarified. In the present experiments, we compared the noncontact AFM images obtained for the Si(100)2x1 reconstructed surface with that for Si(100)2x1:H monohydride surface to investigate the role of chemical reactivity on the surface. It is found that the distance between bright spots is increased by the hydrogen termination. On Si(100)2x1 reconstructed surface, the noncontact AFM atomically resolved the dangling bonds localized outside the silicon dimer with a clear contrast. On the other hand, on Si(100)2x1:H monohydride surface, the noncontact AFM atomically resolved the individual hydrogen atoms on top most layer.

10:20am **SC+SS+EL-ThM7 Making Organic Molecules on Cu(100) and GaAs(100)***, **N.K. Singh**, N. Paris, P. Gatland,* The University of New South Wales, Australia

Alkyl coupling reactions, to form longer chain hydrocarbons, form the basis of many catalysed industrial processes. Surface studies carried out to date to understand the mechanisms by which carbon-carbon bonds form during the coupling process have been restricted to reactions of alkyl halides on coinage metal surfaces. Our recent investigations have shown that GaAs(100), a compound semiconductor, is also capable of catalysing alkyl coupling reactions, which had not been realised previously. Coupling products form irrespective of whether the alkyl groups are derived from alkanethiols or alkyl halides. However, on GaAs(100) the respective higher alkenes form, whereas it is known higher alkanes form on coinage metals. In this paper the surface reactions of a select group of alkanethiols (propanethiol, 1,1,1-trifluoroethanethiol) and alkyl halides (iodoethane, 2-iodo-1,1,1-trifluoroethane) on GaAs(100) and Cu(100), studied by thermal desorption and X-ray photoelectron spectroscopies, will be presented in order to establish the trend in the product mixtures on the two surfaces. We will show that both surfaces exhibit disproportionation and coupling reactions. Disproportionation reactions of the adsorbed alkyl fragments form the corresponding gaseous alkene, alkane and hydrogen. The coupling reactions however on the two surfaces differ. So for example, on Cu(100) CF@sub 3@CH@sub 2@I forms CF@sub 3@CH@sub 2@CH@sub 2@CF@sub 3@ as the coupling product while on GaAs(100) it forms CF@sub 2@=CHCH@sub 2@CF@sub 3@, the corresponding alkene. In the case of coupling reactions of CF@sub 3@CH@sub 2@SH, on Cu(100) CF@sub 3@CH@sub 2@CH@sub 2@CH@sub 3@ is formed while on GaAs(100) , CF@sub 2@=CHCH@sub 2@CH@sub 3@ is formed. These products are inconsistent with the products formed by CF@sub 3@CH@sub 2@I reactions. We will discuss the mechanisms by which these coupling reactions occur, and postulate reasons for the differences in the observed product mixtures on GaAs(100) and Cu(100).

10:40am **SC+SS+EL-ThM8 Adsorption and Thermal Decomposition of Iodoethane on Si(100)-2x1: Kinetically-Favored Adsorbate Ordering***, **A.V. Teplyakov**, K.M. Bulanin, A.G. Shah,* University of Delaware

The adsorption and chemical transformation of iodoethane were studied on a Si(100)-2x1 surface using multiple-internal reflection Fourier-transform infrared spectroscopy (MIR-FTIR). Although ethyl groups are stable on the Si(100)-2x1 surface at room temperature, thermal annealing studies suggest the formation of ethylene, a major hydrocarbon reaction product, accompanied by the loss of hydrogen, which is left on the surface until the temperature of recombinative desorption is reached. Adsorption of iodoethane on Si(100), followed by annealing to 570 K, leaves only hydrogen and iodine on the surface. MIR-FTIR spectroscopy shows that hydrogen is bound in several different types of site at temperatures between 295 K and 570 K. Annealing to higher temperatures produces a distribution dominated by a single hydrogen configuration. First-principles theory and polarization-dependent infrared spectra are consistent with the identification of this configuration as a dimer occupied by one hydrogen and one iodine atom. Calculations show that this configuration is not thermodynamically favored relative to other possible configurations. The observed ordering is attributed to kinetics, a consequence of slow pairing of iodine atoms.

11:00am **SC+SS+EL-ThM9 Are Silicon and Germanium Surfaces Chemically Similar? Reactions of Amines***, **C. Mui**[1], G.T. Wang, J.H. Han, C.B. Musgrave, S.F. Bent,* Stanford University

The organic chemistry at silicon and germanium surfaces has been studied in the past, and the chemical similarity between the two materials is often exploited. In this study, we will present an example in which the surface chemistry of silicon and germanium are notably different. We have used surface infrared spectroscopy and temperature programmed desorption to investigate the chemistry of amines at the Si(100)-2x1 and the Ge(100)-2x1 surfaces. We find that surface reaction of methylamine and dimethylamine on the Si(100)-2x1 surface results in facile N-H dissociation, whereas molecular adsorption occurs on the Ge(100)-2x1 surface. We also show that molecular adsorption of amines on both the Si(100)-2x1 and the Ge(100)-2x1 surfaces occurs through the formation of surface dative bonds which are stable at room temperature. Quantum chemistry calculations are used to explain the observed reactivity difference between the two surfaces. We find that N-H dissociation of dimethylamine is kinetically favored compared to N-CH3 cleavage on both surfaces. However, while N-H dissociation on the Si(100)-2x1 surface is unactivated, the overall activation energy for N-H cleavage on the Ge(100)-2x1 surface is above the vacuum level, explaining the lack of reactivity on the Ge(100)-2x1 surface. We will also discuss our theoretical approach for modeling reactions at semiconductor surfaces, including the effect of surface cluster models and basis sets.

11:20am **SC+SS+EL-ThM10 The Influence of Conjugation in Attachment of @pi@-Electron Containing Organic Molecules to the Si(001) Surface: Acrylonitrile vs. Allyl Cyanide***, **M.P. Schwartz**, S.K. Coulter, R.J. Hamers,* University of Wisconsin-Madison

Organic chemists have developed methods for controlling chemical reactions of complex molecules by defining a broad and detailed set of rules for reactivity. Controlling electron density within a molecule through the use of electron donating or withdrawing groups is a very important way in which to influence product distributions. While a wide variety of unsaturated organic molecules can be tethered to the Si(001) surface, little is known about the role of conjugation of @pi@-electrons in influencing product distribution. In this study, we have investigated the attachment of acrylonitrile (CH2=CH-CN) and allyl cyanide (CH2=CH-CH2-CN) to the Si(001) surface to determine how conjugation of an electron withdrawing group to a vinyl group influences the final surface products. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) measurements show that the attachment chemistry differs significantly for these two molecules. Allyl cyanide adsorbs primarily through the vinyl group while acrylonitrile attaches predominantly via the cyano group. Acetonitrile and benzonitrile were also studied to help determine the nature of the final surface products. The role of conjugation in determining product distributions for attachment of allyl cyanide and acrylonitrile to the Si(001) surface will be discussed.

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[1] **Morton S. Traum Award Finalist**

11:40am **SC+SS+EL-ThM11 Scanning Tunneling Microscopy of a Conjugated {C}3-oligomer on Si(100)**, ***B. Grandidier,*** ISEN, France*; C. Krzeminski, J.P. Nys, C. Delerue, D. Stievenard,* IEMN/ISEN, France*; C. Martineau, P. Blanchard, J. Roncali,* IMMO, France

Scanning tunneling microscopy (STM) has been used to study the adsorption of a {C}3 p-conjugated oligomer on the Si(100) surface. The symmetry of the molecule is resolved with the STM and different conformations are observed. As the oligomer is made up of vinyl groups and aromatic constituents, which are all known to react with the Si(100) surface through cycloaddition reactions, ab initio calculations are performed to determine the occupied molecular orbitals of the free and covalently bound oligomers. The results are compared with the occupied state STM images to characterize the adsorption state of the different conformations.

Surface Science

Room 121 - Session SS1-ThM

Quasicrystals

Moderator: M.A. van Hove, University of California, Berkeley

8:20am **SS1-ThM1 Peter Mark Memorial Award Lecture - Surface Preparation and Electronic Properties of d-AlNiCo***, **E. Rotenberg**[1],* Lawrence Berkeley National Laboratory*; W. Theis, K. Franke,* Free University, Germany*; K. Horn,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany*; P. Gille,* Maximilians-Universitat Munich, Germany **INVITED**

Apart from their striking structural properties, i.e. perfect long range order without translational symmetry, quasicrystals exhibit fascinating physical properties unlike those of ordinary metallic alloys. As the properties of all metals are determined by the valence states near the Fermi level, we have undertaken a program to prepare clean quasicrystalline surfaces and characterize these states by angle-resolved photoemission. The samples were characterized by ESCA, xray photoelectron diffraction (XPD) and LEED. Our k-dependent photoemission intensity maps from the tenfold and two inequivalent twofold surfaces from d-Al@sub 71.8@Ni@sub 14.8@Co@sub 13.4@ shows the existence of dispersing s-p- and d-derived valence states. We use an extension of the concept of the Brillouin zone in order to characterize the observed dispersion. Maps from all three surface orientations yield a consistent picture of free- electron-like constant energy surfaces in 3D k-space. We find the centers of these energy surfaces to be located at the positions of dominant electron diffraction spots as expected from the quasi-Brillouin zone model. Dispersion arises from delocalized quasicrystal valence states, while a large non-dispersing intensity in our spectra could be attributed to either localized states or scattering from the hierarchy of densely spaced Bragg planes in quasicrystals.

9:00am **SS1-ThM3 Structure, Morphology and Dynamics of High Symmetry AlNiCo-Surfaces***, **W. Theis,** H.R. Sharma, K. Franke, A. Riemann, S. Fölsch, K.H. Rieder,* Freie Universität Berlin, Germany*; P. Gille,* Ludwig-Maximilians-Universität München, Germany

Although many aspects of the bulk structure and dynamics of decagonal quasicrystal are well understood, knowledge regarding their surface structure is much more limited. Employing highly surface sensitive elastic He-atom scattering (HAS) and high resolution low energy electron diffraction (SPA-LEED), we have investigated 10- and 2-fold surfaces of Al@sub 71.8@Ni@sub 14.8@Co@sub 13.4@. The observed SPA-LEED and HAS diffraction patterns reveal that the top most surface layer retains the full symmetry extrapolated from the bulk. Both SPA-LEED and HAS show weak superstructure peaks. In the diffraction patterns of the 2-fold surface we observe extremely weak streaks corresponding to a 16 Å periodicity in addition to the strong peaks reflecting the main 8 Å periodicity. The spots in the odd lines of the diffraction pattern are shifted with respect to the even lines by 0.5 Å@sup -1@. He-atom scattering from the 10-fold surface reveals a low corrugation, extremely few defects, an average terrace width in the order of 100 Å, and a predominant step height of 2 Å. Low temperature (5 K) scanning tunneling microscopy (LT-STM) confirms this step morphology showing a high density of rough 2Å-steps without any tendency towards step pairing and revealing regions of two different surface termination and repeating 5-fold symmetric motives. Surface phonons of the 10-fold surface have been investigated by inelastic He-atom scattering. In experiments with cooled and heated samples and He-atom kinetic energies ranging from 8 to 35meV the (acoustic) Rayleigh mode was observed. Strong single phonon signatures are limited to wavevectors q < 0.5 Å@sup -1@ and the phonon linewidths are resolution limited up to q = 0.25 Å@sup -1@, beyond which they increase rapidly, similar to the behavior recently observed in the corresponding bulk phonons. @footnote 1@ @FootnoteText@ @footnote 1@ F. Dugain, et al, Eur. Phys. J. B. 7, 513 (1999).

9:20am **SS1-ThM4 Tribological Properties of Quasicrystals and Quasicrystal Approximants***, **C. Mancinelli,*** Carnegie Mellon University*; J.S. Ko,* Merck & Co.*; A.J. Gellman,* Carnegie Mellon University

An experimental comparison has been made between the properties of the surfaces of an Al@sub70@Pd@sub 21@Mn@sub 9@ quasicrystal and its Al@sub 48@Pd@sub 42@Mn@sub 10@ approximant. This investigation has attempted to identify connections between the quasicrystalline structure and bulk properties. The Al@sub70@Pd@sub 21@Mn@sub 9@ sample was a single grain icosahedral quasicrystal cut to expose its five-fold symmetric (000001) surface. The approximant was polycrystalline @beta@-phase Al@sub70@Pd@sub 42@Mn@sub 10@, which has a CsCl-type cubic structure. Surfaces of both were prepared under ultra-high vacuum (UHV) conditions and then used for comparative measurements of their frictional properties and oxidation rates. The aluminum based quasicrystals and their approximants are oxidized by reaction with O@sub 2@ to form a thin film of aluminum oxide that ultimately passivates their surfaces. The oxidation process was studied using Auger Electron Spectroscopy to measure the oxide film thickness following controlled exposures to both O@sub 2@ and H@sub 2@O. The interesting difference between the two samples is that the rate of oxidation of the approximant is significantly higher than that of the quasicrystal in spite of the fact that the bulk Al concentration of the approximant is lower than that of the quasicrystal. Friction measurements were made under UHV conditions between pairs of quasicrystals and pairs of approximants whose surfaces were either clean or oxidized to varying degrees. The friction measurements were made between pairs of clean surfaces and between pairs of surfaces exposed to controlled oxidation. The friction between pairs of the approximant surfaces is roughly twice that measured between the quasicrystal surfaces under all conditions of surface oxidation. The results of this work do suggest that there is a direction connection between the quasicrystalline structure and low friction.

9:40am **SS1-ThM5 Surface Properties of Quasicrystals***, **P.A. Thiel,*** Iowa State University **INVITED**

There has been a systematic progression of knowledge, over the past 10 years, concerning the atomic arrangements and compositions at surfaces of bulk quasicrystals. Our group has been particularly involved in studying surfaces of the icosahedral aluminum-rich phases, both in ultrahigh vacuum and in air. The understanding of the surface structure of these materials is currently at a point where, we believe, it can be used as a springboard toward understanding more complex phenomena. Following a review of the picture that has evolved for the native surfaces in vacuum and in air, we will discuss more recent results for friction, wetting, and epitaxy.

10:20am **SS1-ThM7 Auger Spectroscopy and the Electronic Structure of Quasicrystals***, **V. Fournèe,** J.W. Anderegg, A.R. Ross, T.A. Lograsso, P.A. Thiel,* Iowa State University

So far, the electronic structure of QC has been probed primarily by photoelectron and x-ray spectroscopies. These studies mainly focussed on the existence of a structure induced minimum of the density of states located at the Fermi level, the so-called pseudogap. Auger spectroscopy, on the other hand, can yield unique insight into important aspects of the electronic structure of alloys such as screening and electron correlation effects. Here we will present our experimental work on the transition metals LMM Auger lines in several quasicrystalline phases, the Al-Pd-Mn and Al-Cu-Fe icosahedral QCs and the Al-Ni-Co decagonal QC. This include the core-core-valence and the core-valence-valence Auger spectra. From the line shape, line splitting and energies of the Auger spectra, it is possible to derive empirical parameters correlated with the extent of quasiatomic or bandlike behavior, which depends on the relationship between the local DOS and the value of the on-site correlation energy. Our first results in the i-Al-Pd-Mn clearly shows that the Mn-L3M45M45 has a bandlike behavior and reflects the self-convolution of the Mn-3d valence band. The width of the Mn-3d band is quite narrow in the QC, as compared to pure Mn. We also found a decrease of the 3d-containing Auger transition rates in the QC relative to the metal. This could be due to an increased localization of the 3d states in the quasicrystals, that will lower the probability for a 3d electron to fill a 2p photohole. This is consistent with the reduction of the

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[1] **Peter Mark Memorial Award Winner**

intrinsic width of the Mn 2p3/2 core level observed by photoemission spectroscopy.

10:40am **SS1-ThM8 Nucleation and Growth of Al and Ag Thin Films on Five-fold Surface of Icosahedral Quasicrystals**, ***T. Cai***, *V. Fournee, T.A. Lograsso, A.R. Ross, P.A. Thiel,* Iowa State University

Aluminium and silver are deposited on the five-fold surface of icosahedral Al-Cu-Fe and Al-Pd-Mn quasicrystals. The nucleation and growth of thin metal films on quasicrystalline surface are studied using scanning tunnelling microscopy. Our first results on Al films deposited on Al-Cu-Fe show that, at low coverage, Al atoms form pentagonal stars, all adopting the same orientation, though with no evidence of order between the Al pentagonal stars. As Al coverage is increased, but still within the submonolayer regime, the density of Al pentagonal stars increases. The five-fold symmetry of the quasicrystalline substrate is responsible for arranging deposited atoms with a local five-fold symmetry, which is incompatible with the translation periodicity of the cubic lattice of the individual elements. With scanning tunnelling microscope, we expect to observe directly the transition from a pentagonal symmetry to the face-centred cubic symmetry as the metallic film develops on the quasicrystalline surface.

11:00am **SS1-ThM9 Accessing the Role of Net Planes in Decagonal Al-Ni-Co**, ***C.J. Jenks***, *J. Bjergaard, P.A. Thiel, P. Canfield,* Iowa State University; *A. Cervellino, W. Steurer,* ETH-Zurich, Switzerland

Net planes linking the periodic and quasiperiodic directions in decagonal Al-Ni-Co are discussed. These net planes are thought to play a critical role in the stability and growth of decagonal quasicrystals. To explore their potential roles we have studied single grain surfaces of decagonal Al-Ni-Co. We have used surface analytical techniques to study surface morphology which sheds light on the structural stability of these planes.

Surface Science
Room 122 - Session SS2-ThM

Electronic Structure II

Moderator: H. Petek, University of Pittsburgh

8:40am **SS2-ThM2 Fermi Surface Evolution of Ag(111) Films Grown onto Si(111) Surfaces**, *V. Perez-Dieste,* LURE, France; *J.F. Sanchez-Royo,* LURE and ICMUV, France; *J. Avila,* LURE and ICMM, France; *M. Izquierdo, L. Roca, A. Tejeda,* LURE, France; ***M.C. Asensio,*** LURE and ICMM, France

Growth of metal films on semiconductor substrates has been the subject of extensive experimental and theoretical studies over the last decades. The determination of the metallization onset at the semiconductor interfaces and the obtention of thin single-crystal metal films, only a few atomic layers thick with atomically flat surfaces, are important goals because of their consequences on the manufacture of integrated circuits and nanosized devices. In this work, we investigate the epitaxial growth of silver overlayers on reconstructed Si(111) surfaces studied by LEED and Photoelectron Diffraction (PhD). The electronic properties of these films have been investigated by high energy resolution Angle-Resolved Photoemission (ARPES) with a synchrotron radiation source. Particular attention has been paid to the determination, by ARPES, of the spectral weight at the Fermi level along large extensions of the reciprocal space of the investigated films, from which the Fermi surface (FS) can be extracted. The evolution of the FS and the valence-band structure as a function of the silver coverage could be measured at several metal coverages. In the submonolayer regime, very localized interface-derived spectral features dominate the density of states at the Fermi level, whereas in the intermediate regime, a complex mixture of states from both the interface and the metallic silver film defines the incipient FS contours. A well defined bulk-like silver FS could be identified already at interfaces of a few Ag monolayers. However, the symmetry of these bulk-like FS contours showed sixfold symmetry rather than the threefold symmetry, characteristic of a Ag(111) single crystal. By PhD, it has been demonstrated that is due to the existence of two domains rotated 60Âº silver metallic overlayers.

9:00am **SS2-ThM3 Ultrathin Epitaxial Mg Films on Si(111): Quantum Size Effects**, *L. Aballe,* ***C. Rogero***, *K. Horn,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

We demonstrate, using angle-resolved photoelectron spectroscopy and LEED, that highly perfect ultrathin epitaxial Mg(0001) films can be grown on Si(111) using low temperature deposition and annealing. This is in contrast to films grown at room temperature which present an interfacial silicide and subsequent growth of a disordered Mg metallic film. The wave-vector dependent electronic structure of the well-ordered films is investigated in detail with photoelectron spectroscopy, as a function of overlayer thickness. The spectra exhibit a number of thickness-dependent discrete peaks in the region of the magnesium s-p band for films up to 40 monolayers thick. These are caused by electron confinement within the Mg overlayer, and can be identified as quantum well resonances derived from the magnesium s-p band. These quantum well resonances (QWR) are interpreted in terms of the phase-accumulation model, and the Mg band structure is found to account for all the main features in the spectra. An estimation of the decay length of the Mg(0001) surface state wave function is obtained from its dependence of binding energy on film thickness. The in-plane dispersion of the QWR for films of different thicknesses is measured and analyzed along the surface Brillouin zone. The data point to a strain-driven thickness-dependent structural transition at a critical thickness of about 20 Mg monolayers. The dependence of spectral intensity on photon energy in the range of the Mg bulk and multipole plasmon energies demonstrates the effect of field enhancement in the Mg film.

9:20am **SS2-ThM4 Resonant Photoemission Investigation of the Electronic Structure of Plutonium**, ***J.G. Tobin***, *D.A. Arena,* Lawrence Livermore National Laboratory; *J. Terry, R.K. Schulze, J.D. Farr, T. Zocco,* Los Alamos National Laboratory; *K. Heinzelman, E. Rotenberg, D. Shuh,* Lawrence Berkeley National Laboratory; *G. van der Laan,* Daresbury Lab, UK

The valence electronic structures of the actinide metals and alloys in general and plutonium (Pu) in particular remain mired in controversy. Interestingly, the various phases of Pu metal provide a mirocosm of the metallic actinides as a whole. Thus, unravelling the nuances of the interplay of electronic and geometric structures in Pu will illuminate the properties of all transuranic metals. In a sense, the behavior of the Pu 5f electrons is completely counter-intuitive. The dense phase, a, has some semblance of delocalization in the 5f valence bands and can be treated theoretically within single electron models such as the Local Density Approximation (LDA). The a phase is monoclinic, which is a low symmetry ordering. The less dense d-phase is fcc and exhibits evidence of localized and/or correlated electronic behavior. Experimental Resonant Photoemission (ResPes) results for a- Pu and d- Pu bulk samples will be presented and compared to the results of an atomic model calculation. Both Pu samples exhibit limited agreement with the atomic model calculations. As expected, a- Pu appears to have more 5f valence band delocalization than d-Pu. Evidence of an enhanced sensitivity to surface corruption, by using synchrotron radiation as the excitation, will be presented. This work was performed under the auspices of the U.S Department of Energy by Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48. Los Alamos National Laboratory is operated by the University of California under Contract No. W-7405- ENG-36. Experiments were carried out at the Spectromicroscopy Facility (Beamline 7.0) at the Advanced Light Source, built and supported by the U.S. Department of Energy. The Advanced Light Source and DKS are supported by the Director, Office of Science, Office of Basic Energy Sciences, Matl. and Chem. Sciences Divisions, of the U.S. DOE under Contract No. DE-AC03-76SF00098 at Lawrence Berkeley National Laboratory.

9:40am **SS2-ThM5 Visualization of the Electronic Structure of Metal Surfaces with Scanning Tunneling Spectroscopy**, ***J.I. Pascual***, Fritz-Haber-Institut der Max-Planck Gesellschaft, Germany; *Z. Song,* Dalian Institute of Chemical Physics. China; *J.J. Jackiw,* Pennsylvania State University; *M. Hansmann, G. Ceballos, H. Conrad, K. Horn, H.-P. Rust,* Fritz-Haber-Institut der Max-Planck Gesellschaft, Germany

In this presentation we analyze the electronic structure of several metal surfaces with an in-creasing level of complexity: from the (111) sur-faces of noble metals, with isotropic s-p states, to anisotropic alloy surfaces like NiAl(110), where the influence of Ni d-states dominates its elec-tronic structure in the proximity of the Fermi level. The measurements are done in a low temperature scanning tunneling microscope, where the energy resolution and stability are greatly improved. The spatial dependence of the differential tunnel con-ductance in the proximity of scattering potentials like defect sites or step edges offers a direct way to access structural information on the electronic states of the surface. There, the electron wave phase is fixed at the defect position, producing oscillations in the spatial shape of the density of states in the defect vicinity. The wavelength of these oscillations in real space can be easily transformed to reciprocal space information by means of a Fourier transformation.@footnote 1@ We are going to show the capabilities of this transformation by analyzing surface states on both, the isotropic and anisotropic surface states. Band gap edges also may produce oscillations in the density of states, and therefore, are also ac-cessible. By measuring the differential conduc-tance in a large range of energies we reconstruct the states' topology in the reciprocal space. The energy range is not limited to the proximity of the Fermi energy: we probe states up to the vacuum level. Above this point we also resolve information about the surface density of states by analyzing the shape of the field emission resonances. . @FootnoteText@@footnote 1@L. Petersen et al. Phys. Rev. B 57, R5868 (1998).

10:00am **SS2-ThM6 Temperature-Dependent Fermi Gap Opening in the c(6X4)-C@sub 60@/Ag(100) Two-Dimensional Superstructure***, **M. Sancrotti**, C. Cepek, I. Vobornik,* Laboratorio Nazionale TASC-INFM, Italy*; A. Goldoni,* Sincrotrone Trieste, Italy*; E. Magnano,* Laboratorio Nazionale TASC-INFM, Italy*; G. Selvaggi,* Universita' di Modena, Italy*; J. Kröger,* Zürich Universität, Switzerland*; G. Panaccione, G. Rossi,* Laboratorio Nazionale TASC-INFM, Italy

The interest in fullerene-based films, their surfaces, and related low-dimensional systems has been recently renewed for example by the discovery that superconductivity persists at surfaces of A@sub 3@C@sub 60@ films@footnote 1@ and by the possibility of achieving a critical temperature as high as 52 K in hole-doped C@sub 60@ single crystals.@footnote 2@ The possibility of controlling at a fine scale the charge state of single C@sub 60@ molecules and the buckyball-buckyball distance makes the fullerene-based films extremely charming for a wide range of applications. In addition, chemical and physical properties of low-dimensional C@sub 60@-based layers may be considered superior to the bulk materials, prepared by means of standard intercalation methods and plagued by the presence of multi-phases. Here we report on a high-resolution angle integrated photoemission study@footnote 3@ of one monolayer of C@sub 60@ chemisorbed on Ag(100). The results show the reversible opening of a gap at the Fermi level at temperatures 25 @<=@ T @<=@ 300 K. The gap reaches a maximum value of 10 meV at T @<=@ 70 K. This finding is a first evidence of an electronic phase transition in C@sub 60@ monolayers and has implications on the ongoing debate about surface superconductivity in C@sub 60@-based bulk materials. @FootnoteText@ @footnote 1@ R. Hesper, L.H. Tjeng, A. Heeres, and G.A. Sawatzky, Phys. Rev. Lett. 85 (2000) 1970 @footnote 2@ J.H. Schön, Ch. Kloc, R.C. Haddon, and B. Batlogg, Science 288 (2000) 656 @footnote 3@ C. Cepek, I. Vobornik, A. Goldoni, E. Magnano, G. Selvaggi, J. Kröger, G. Panaccione, G. Rossi, and M. Sancrotti, Phys. Rev. Lett. 86 (2001) 3100

10:20am **SS2-ThM7 Electronic Transport through Surface-state Bands***, **S. Hasegawa**,* University of Tokyo, Japan **INVITED**

Surface states that are inherent in surface superstructures, provide unique platforms for studying low-dimensional electron systems, exhibiting some aspects of many-body effects, in phase transitions, for example. Electronic transport is a key for such physics, too. First, I present direct detections of electrical transport through the surface-state bands on silicon, by in-situ measurements in UHV with macroscopic four-point probes,@footnote 1@ microscopic ones,@footnote 2,3@ and four-tip STM.@footnote 4@ The influences of atomic steps and domain boundaries on the conductivity were directly measured. Next, I present characteristic changes in surface conductivity at a surface phase transition.@footnote 5@ A Si(111)-8x2-In surface at 100K is believed to be a charge-density-wave (CDW) phase.@footnote 6@ By adding small amounts of impurity atoms on it, the CDW phase was destroyed, accompanied with steep increases in conductivity. This means that the metalicity of the surface is recovered by this change; the impurity atoms act as electronic disturbers. @FootnoteText@ @footnote 1@ S. Hasegawa, et al., Prog. Surf. Scie. 60 (1999) 89. @footnote 2@ I. Shiraki, et al., Surf. Rev. Lett. 7 (2000) 533. @footnote 3@ C. L. Petersen, et al., Appl. Phys. Lett. 77 (2000) 3782. @footnote 4@ I. Shiraki, et al., Surf. Scie. (2001) in press. @footnote 5@ S. V. Ryjkov, et al., Surf. Scie (2001) in press. @footnote 6@ H.-W. Yeom, et al., Phys. Rev. Lett. 82 (1999) 4898.

11:00am **SS2-ThM9 Electronic Structure of the Alkali Halide-metal Interfaces: LiCl(100)/ Cu(100)***, **M. Kiguchi**, H. Inoue, K. Saiki, A. Koma,* The University of Tokyo, Japan

When an insulator film is prepared in the close vicinity of a metal surface, a novel phase is formed whose property may differ from the bulk one. It is suggested that the band gap is reduced for an insulating thin film on a metal substrate, due to the presence of the dielectric boundary and the overlayer reduced dimensionally. However, the large difference of chemical bond between metals and insulators makes it difficult to form a well ordered interface. The electronic structure of the insulator-metal interface has been little studied. Recently, we have succeeded in growing a single-crystalline LiCl film on Cu(100) in a layer-by-layer fashion. In the present work, we have studied the electronic structure of LiCl film on Cu(100) using EELS (electron energy loss spectroscopy) and UPS (ultraviolet photoelectron spectroscopy), as a model system of alkali halide-metal interface. The EEL spectrum(Ep=60 eV) shows clear band gap region from 0 eV to 7 eV. The band gap energy did not change for the LiCl thickness from 1 ML to 20 ML. In addition, the 61 eV loss peak observed in the EELS (Ep=200eV) did not change with the thickness. The result of EELS indicates that relative position of the conduction band to the valence band and to the Li 1s core band was unchanged. In the result of UPS, on the other hand, the valence band showed upward shift with decreasing film thickness. The results of EELS and UPS suggest the occurrence of the bend bending in ionic layers.

11:20am **SS2-ThM10 Theoretical Analysis of Field Emission from Atomically Sharp Al Tips***, **Y. Gohda**,* The University of Tokyo, and CREST, Japan Science and Technology Corp., Japan*; S. Watanabe,* The University of Tokyo, and CREST, Japan Science and Technology Corp.

Well-conditioned tips, which end with a single atom, are of current interest, because they produce self-collimated, coherent electron beams, total energy distribution (TED) of which can have multiple peaks (MP).@footnote 1,2@ However, the origin of the MP in TED has been controversial and thus has not been understood well: Binh et al. claimed that they had observed MP from pure W(111) surface with single-atom protrusion,@footnote 1@ while Yu et al. claimed that carburization was essential in observing MP from metal-carbide protrusions.@footnote 2@ In the present work, field emission from Al(100) surface having single-atom protrusion without any impurity is analyzed employing the method newly developed by Gohda et al.,@footnote 3@ which is based on the self-consistent density functional theory including scattering states. We have found that MP in TED of field emission current becomes remarkable as the local potential barrier in front of the topmost Al atom dissapears with increase in applied field strength. We have also clarified that the peak below the Fermi energy is attributed to localized sates at the topmost Al atom, while the peak at the Fermi energy comes from delocalized states. @FootnoteText@ @footnote 1@ V. T. Binh et al., Phys. Rev. Lett. 69, 2527 (1992). @footnote 2@ M. L. Yu et al., Phys. Rev. Lett. 77, 1636 (1996). @footnote 3@ Y. Gohda et al., Phys. Rev. Lett. 85, 1750 (2000).

Thin Films
Room 123 - Session TF+BI-ThM
Bioactive and Organic/Inorganic Thin Films

Moderator: L. Hultman, Linköping University, Sweden

8:20am **TF+BI-ThM1 Self-aligned Deposition and Patterning of Biologically-active Polymer Thin Films***, **B.H. Augustine**, S.M. Ramirez, O.D. Lees,* James Madison University

High-resolution patterning and microfabrication of polymeric and other soft materials is challenging since traditional photolithographic methods require organic solvents to remove photoresist. These solvents typically also dissolve or degrade biological and polymeric surfaces which one might pattern. We report selective dewetting using microcontact printing (µ-CP), micromolding in capillaries (MIMIC), and solvent assisted micromolding (SAMIM) techniques to pattern thin films of the biodegradable copolymer, poly-3-hydroxybutyrate-co-3-hydroxyvalerate [P(3HB-3HV)] onto glass, silicon, and Au coated silicon substrates. Film thicknesses range from 20 mn to over 700 nm, with minimum feature sizes as small as 3 µm. Dense 100 nm thick films with sub-10 µm features can be patterned in as few as two minutes for the entire processing resulting in potentially high throughput processing. Thin film microstructure can be dramatically changed by controlling deposition parameters such as solvent concentration, feature aspect ratio, and polarity of the solvent. While we report microfabrication techniqes for a specific biodegradable polymer system, we will also comment on extending these techniques to other polymer systems and the issues affecting the profound change in polymer microstructure using these three different patterning techniques.

9:00am **TF+BI-ThM3 Desorption and Processing of Bioactive Thin Films***, **A. Chilkoti**,* Duke University **INVITED**

I will describe methods to micro- and nano-pattern proteins and other biological ligands onto self-assembled monolayers (SAMs) and polymers for application in multianalyte biosensors, patterned biomaterials, and protein chips. These methods include: (1) Light-activated micropatterning (LAMP), which exploits spatially precise, light-activated deprotection of affinity ligands on functionalized SAMs to achieve step-and-repeat patterning of multiple biomolecules. (2) Microstamping onto activated polymer surfaces (MAPS), which involves surface-selective functionalization of polymers, followed by microcontact printing of reactive biological ligands. (3) Thermodynamically addressable reversible patterning (TRAP) which uses patterned domains with different surface energies as a thermodynamic address to direct the attachment of proteins and other biomolecules from solution. TRAP functions by the selective adsorption of nanoclusters of an elastin fusion protein above its phase transition temperature specifically on patterned hydrophobic regions, but not on a hydrophilic background. Unlike other methods for protein patterning, TRAP is reversible, and modulating the solution environment (e.g., T, ionic strength), can erase protein patterns. A theme illustrated by this talk will be the interdisciplinary convergence of surface chemistry and spectroscopic characterization (XPS, TOF-SIMS, and evanescent optical techniques) with molecular biology.

9:40am **TF+BI-ThM5 Nano-scale Fabrication Using Organic Thin Films*, C.B. Gorman,*** North Carolina State University **INVITED**

We will show how a combination of lithographic methods on organic self-assembled monolayers (SAMs) can be used to form chemically well-defined, patterned surfaces. These surfaces can form the basis of nanometer-scale, molecular electronic devices. The talk will focus on (1)the engineering and the chemistry behind nanometer scale lithography on SAMs including an assessment of its strengths and limitations, (2) why the control of chemical functionality is so important for a true, nanometer-scale process and (3) demonstration of new, molecular electronic behaviors with potential applicability in devices.

10:20am **TF+BI-ThM7 Hot-Filament Chemical Vapor Deposition of Fluorocarbon-Organosilicon Copolymer Thin Films*, S.K. Murthy,*** *K.K. Gleason,* Massachusetts Institute of Technology

Hot-filament chemical vapor deposition, a non-plasma technique, has been used to deposit copolymer thin films consisting of fluorocarbon (CF@sub 2@) groups and organosilicon groups (Si(CH@sub 3@)@sub 2@ - O) at rates of approximately 250 angstroms/min. The synthesis of such copolymers by solution chemistry techniques is difficult since one component (PTFE) is normally synthesized by free radical polymerization techniques and the other (PDMS) by ionic polymerization methods. The presence of covalent bonds between the fluorocarbon and organosilicon moieties in the thin films has been confirmed by Infrared, X-Ray Photoelectron (XPS) and solid-state @super 29@Si, @super 19@F, and @super 13@C Nuclear Magnetic Resonance (NMR) spectroscopy. These techniques also indicate retention of methyl groups from the siloxane precursor. The XPS data shows that all of the silicon present in the films is in the +2 oxidation state and that the ratio of silicon to CF@sub 2@ groups is approximately 1:0.86 based on atomic composition. Further, the NMR data suggest that the copolymer films are blocky in nature, consisting of networked chains having multiple fluorocarbon groups interspersed between siloxane groups. Atomic Force Microscopy of the films showed that the roughness of these copolymer films is in-between that of homopolymeric fluorocarbon and organosilicon films made by the same technique.

10:40am **TF+BI-ThM8 Polyatomic Ion Deposition of Gradient Thin Films: A New Method for Combinatorial Materials*, L. Hanley,*** *M.B.J. Wijesundara, E.R. Fuoco,* University of Illinois at Chicago

Beams of gaseous ions are used for the growth and modification of interfaces in a wide variety of applications. For example, we have previously shown that mass-selected CF@sub3@@super+@, C@sub3@F@sub5@@super+@, and Si@sub2@O(CH@sub3@)@sub3@@super+@ ions can be employed for the growth and modification of organic thin films on polymer and metal surfaces.@footnote1@We demonstrate here that polyatomic ion beams can also be employed to create chemical gradient thin films by variation of the ion fluence across the substrate. We use mass-selected C@sub3@F@sub5@@super+@ ion deposition in vacuum to create a fluorocarbon gradient film on a polymethylmethacrylate substrate. X-ray photoelectron spectroscopy shows a continuous change in the surface chemistry from that of the native polymer to a fluorocarbon film. The contact angle varies from ~75° to ~95° across the gradient surface. We also examine the production of fluorocarbon films on polystyrene, silicon, and aluminum surfaces from C@sub3@F@sub5@@super+@ ions. Finally, we discuss the general feasibility of producing chemical gradients surfaces from polyatomic ion beams. @footnote1@M.B.J. Wijesundara, Y. Ji, B. Ni, S.B. Sinnott, L. Hanley, J. Appl. Phys. 88 (2000) 5004

11:00am **TF+BI-ThM9 Plasma Sputtering Deposition of Metals on PAMAM Dendrimer Monolayer***, A. Rar, M. Curry, F. Xu, J.A. Barnard,* ***S.C. Street,*** University of Alabama

A number of nanotechnology applications require development of thin, flat surface films with well-regulated mechanical and tribological properties. A promising approach for this is metal layer deposition on PAMAM dendrimer underlayers. Previously, we demonstrated improvement in mechanical and morphological properties for Au, Co, and Cr films deposited by evaporation onto dendrimer self-assembled monolayers. In this paper we will discuss formation of metallic layers on dendrimer by plasma sputtering deposition. We will show the influence of higher incoming kinetic energy of the metal atoms on dendrimer structure and chemical changes at the interface. The evolution of the dendrimer interlayer during metal deposition was analyzed with XRR, the surface morphology of deposited films with AFM, the chemical interaction between deposited metal and dendrimers with XPS and RAIRS. Thin Cr layers obtained by plasma sputtering interact with the dendrimer interlayer in essentially the same way as films deposited by evaporation. Significant differences were found for Cu/dendrimer layers prepared by plasma sputtering deposition compared to less energetic thermal evaporation. In the first case more than 1/3 of the nitrogen atoms in the dendrimer adlayer form nitride-like chemical states. Thermal evaporation shows less pronounced influence on the N1s XPS peak.

Tribology
Room 132 - Session TR-ThM

Tribological Surface Engineering for Lubrication & Wear Resistance

Moderator: W.-D. Munz, Sheffield Hallam University

8:20am **TR-ThM1 Tribological Surface Engineering for Lubrication and Wear Resistance*, L.E. Seitzman,*** Caterpillar Inc. **INVITED**

Tribological Surface Engineering is the art of modifying a materials surface or near-surface by some means in order to achieve a desired friction or wear response of the material. One method available to surface engineers involves the application of metallurgical coatings, grown by one of several plasma-assisted vapor deposition processes. Such metallurgical coatings, usually only a few micrometers thick, have been used to improve the performance of cutting and forming tools and dies for many years. More recently, these coating have been successfully applied to mechanical components in order to extend life or to increase productivity of machines. The performance of the coatings depends on a number of factors, including chemistry, microstructure, surface texture and, of course, adhesion. We will illustrate some of these dependencies for coatings subjected to sliding. As a general rule, metallurgical coatings that provide the best friction reduction exhibit short wear life, and coatings with long wear life rarely reduce friction. The reason for this dichotomy and how it provides direction for the R&D community will be discussed.

9:00am **TR-ThM3 Optimization of Wear-resistant Coating Architecture using Finite Element Analysis*, T.Z. Gorishnyy,*** *M.S. Aouadi, L. Olson, S.L. Rohde,* University of Nebraska - Lincoln

Chromium nitride based single layer, bilayer and multilayer coatings were deposited by unbalanced reactive magnetron sputtering on A2 steel and aluminium substrates. Their wear rates were measured using pin-on-disk testing under normal loads of 4 N and 10 N for Aluminum and A2 steel substrates respectively. Finite element analysis (FEA) was utilized to investigate stress distributions in film-substrate systems under conditions, which related to those of the actual wear tests. Two-dimensional asymmetrical models were created for every coating-substrate architecture tested. The FEA results were compared with analytical solutions for Hertzian contacts with and without frictional effects. A good fit was observed. Fracture mechanics in conjunction with FEA data was used to interpret differences in wear rates for different samples. The following possible causes of fracture were considered: (1) failure in individual layers; (2) delamination of multilayered films due to high in-plane interfacial stresses; (3) failure due to crack propagation at film-substrate interface and (4) failure as a result of film buckling.

9:20am **TR-ThM4 Solution-Assisted Tribological Modification of Surfaces Using an Atomic Force Microscope***, R. Hariadi, S.C. Langford,* ***J.T. Dickinson,*** Washington State University

When a surface is subjected to tribological loading, bonds experience time dependent distortions and spatial deformations. In the presence of simultaneous chemical stimulation (e.g., from a solution), this can lead to bond breaking, bond formation, and nuclear rearrangement. We present new studies of combining mechanical and chemical stimuli in model tribological and structural systems, particularly under conditions of solution supersaturation. Thermodynamically, the system tends towards deposition or crystal growth; we show that nucleation and growth on the surface can be controlled on the nanometer size scale using simultaneous mechanical stimulation with an AFM tip. New details of this process are presented with strong support of suggested models using analysis of small perturbations in the frictional force. Careful analysis of the"noise" in the cantilever motion during contact scanning shows that on single crystal surfaces we are very sensitive to the presence of sub-critical cluster formation and re-dissolution, we find that the amplitude of the noise increases by factors of 2-4. We take this as indirect evidence for the presence of these precursors to recrystallization. Furthermore, rich noise spectra are observed on crystal surfaces with low symmetry when one changes the scan directionâ€"we observe modulated signals at frequencies corresponding to calculated times between asperity-lattice row encounters. Again, under supersaturation, the noise levels rise in comparison with pure solvent. Finally, we present structures and surface modifications that can be induced by these mechanical/chemical synergisms.

9:40am **TR-ThM5 Low Frictional Force Coating of Boron Nitride - Copper Complex for Ultra High Vacuum by Magnetron Co-sputtering Technique***,* ***M. Goto****, A. Kasahara, M. Tosa, K. Yoshihara,* National Institute for Materials Science, Japan

Boron nitride - copper complex (BN/Cu) coating films were synthesized by a magnetron co-sputter technique. The characteristics of the films such as surface energy, internal stress, surface morphology, elements configuration and adhesion force were measured. Frictional force of the coating films was also measured with a self-made vacuum-friction measuring system from an atmospheric pressure to the pressure of 10-7 Pa. Frictional coefficients of the BN/Cu films as low as 0.1 is achieved in UHV region. It was found that the mixture structure of boron nitride with copper formed under different discharge time was most effective to change the frictional force. This technique is applicable to produce low-frictional force materials for ultra high vacuum system.

10:20am **TR-ThM7 Aging Evaluations of MoS@sub 2@-Containing Lubricants@footnote 1@***,* ***D.E. Peebles****, M.T. Dugger, W.F. McNamara, J.A. Ohlhausen, E.H. Sorroche,* Sandia National Laboratories

Many solid film lubricants and self-lubricating materials utilize MoS@sub 2@ as the active lubricant phase. Oxidation of MoS@sub 2@ produces MoO@sub 3@ and surface sulfate species, which do not possess the same lubrication properties as MoS@sub 2@. However, the rate and mechanism for oxidation of MoS@sub 2@ is a strong function of the surrounding matrix material and the ambient oxidizing species. This work will review aging studies that have been performed for materials containing MoS@sub 2@ particles in polyimide and epoxy resin matrices. This work will illustrate the aging process from the viewpoint of chemical and performance modifications as a function of oxidation in a variety of atmospheric environments. Evaluations of the chemical state of the lubricant material are assessed by detailed surface chemical studies by x-ray photoelectron spectroscopy, while lubricant performance is assessed by pin-on-disk testing. The understanding of lubricant aging mechanisms obtained from these studies is being used to develop age-aware performance models for electromechanical devices. @FootnoteText@ @footnote 1@Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

11:00am **TR-ThM9 Diamond-Like Carbon Nanocontacts***,* ***R.W. Carpick****, J.R. VanLangedon, E.H. Wilson, K. Sridharan,* University of Wisconsin - Madison

Wear-resistant low-friction coatings are of interest for a variety of applications from automotive engines to sub-micron machines. One particularly important coating is diamond-like carbon (DLC), which can possess mechanical properties approaching those of diamond. We have used atomic force microscopy to study the nanotribological properties of DLC as a function of preparation to investigate the mechanisms that underlie ultralow friction and wear. Furthermore, we have fabricated nano-asperities by coating the tips of atomic force microscope cantilevers with DLC. The unique coating process, plasma-source ion deposition, produces a high-quality conformal coating of DLC. By placing this asperity in contact with a DLC-coated substrate, we are able to measure, for the first time, the mechanical and frictional properties of DLC/DLC interfaces at the nano-scale. We will discuss the fundamental relations governing friction for this interface.

Vacuum Science & Technology
Room 125 - Session VST-ThM

Pressure & Flow Measurement Instruments & Their Calibration

Moderator: K.M. Welch, Consultant

8:20am **VST-ThM1 Is the Effective Accommodation Coefficient of the Spinning Rotor Gauge Temperature Dependent?***,* ***K.J. Jousten,*** Physikalisch-Technische Bundesanstalt, Germany

The spinning rotor gauge (SRG) is a vacuum meter for the range 10@super -4@ Pa -to- 1Pa with good long term stability; therefore it is widely used as reference standard in calibration services. The calibration constant of the SRG is the effective accommodation coefficient @sigma@ valued around 1. This accommodation coefficient of the gas particles to the rotor is considered temperature independent for the normal operational temperatures 18°C -to- 30°C. We have carried out investigations that show that @sigma@ of an unbaked rotor (which is not unusual in calibration services) is temperature dependent. The operational temperature of the SRG could be varied from 16°C -to- 40°C. Typical relative changes of @sigma@ were 0.1% per 3 degree change of temperature, but larger changes were also observed. It will be discussed, if the changes are related to a change of H@sub 2@O coverage of the rotor.

9:00am **VST-ThM3 Using Capacitance Diaphragm Gauges at Different Temperatures***,* ***J.C. Greenwood,*** National Physical Laboratory, U.K., United kingdom*; U.M.E. Christmas,* University of Surrey, UK

Capacitance diaphragm gauges are used in many industrial applications for absolute pressure measurements. The gauges are heated to improve stability but this procedure introduces thermal transpiration effects due to the temperature difference between the gauge head and the vacuum system. Calibration incorporates these effects although the calibration data are only valid when the gauge is operated at the same temperature as that during calibration. In practice, different temperatures are used and systematic errors are introduced. The calibration data can be represented using a thermal transpiration model but it is not clear whether such a model provides an adequate method of predicting performance at different temperatures. Two capacitance diaphragm gauges have been calibrated over the pressure range 0.02 Pa to 133 Pa at three different ambient temperatures and the calibration data at temperatures of 291K and 301K have been compared with the data predicted by applying a thermal transpiration model to data collected at 293K. The uncertainty associated with making such a prediction is evaluated.

9:40am **VST-ThM5 Low-pressure Capacitiance Diaphragm Gage Measurements and Characteristics***, S Lu,* ***S.A. Tison,*** Mykrolis formerly Millipore Microelectronics

Low-pressure measurement is critical for many applications within the vacuum community. The International Technology Roadmap for Semiconductors identifies a number of areas of process improvement required to meet the semiconductor device characteristics for the next five years. The requirements include better sidewall etch control and selectivity, processing of high and low k dielectric films and adequate process control to improve statistical process variations. Many of the critical processes occur at pressures below 100 mTorr where pressure measurement is most difficult. Traditionally, vacuum process measurements have been referenced to capacitance diaphragm gages (CDGs) sometimes called capacitance manometers. Characteristics of these instruments such as zero drift and mechanical creep, while being acceptable for higher range CDGs become more problematic for low-range CDGs where these effects become the major source of measurement error and process variability. This study evaluates the performance of three CDG designs which attempt to improve low-pressure performance. The data shows that maximizing the sensor sensitivity, may result in more mechanical drift and a balance between mechanical sensitivity and electrical gain is the optimum solution for overall instrument performance.

10:00am **VST-ThM6 Static Gas Expansion Method as High-accuracy Primary Pressure Standard*, W. Jitschin,*** University of Applied Sciences, Germany

For the calibration of vacuum gauges in the range of medium and high vacuum, the method of static gas expansion is widely adopted as high-accuracy primary method. In this method, gas is expanded from a small vessel into a large one, whereby the pressure is reduced according to the volume increase. Uncertainties of the generated pressure arise from uncertainties of initial pressure, volume ratio of both vessels, real gas behavior, and thermal effects. As comes out from the uncertainty budget of a conventional expansion apparatus, the dominant contribution stems from temperature effects. For example, a typical temperature uncertainty of 0.3K gives a relative pressure uncertainty of 0.1% . In order to obtain a substantially improved accuracy, the whole apparatus was immersed in a circulated, temperature controlled water bath. This measure resulted in a tenfold improved temperature stability of the vessel walls, i.e. better than 0.03K. Furthermore, thermal effects caused by the thermodynamic process of gas expansion were investigated. In fact, the gas in the small vessel cools by as much as -200K. As our experimental and theoretical studies reveal, the thermal equilibrium between the gas and the vessel walls is reached with time constants of the order of seconds, depending on gas species and pressure. Accordingly, after a typical waiting time of about 1 minute after filling the small vessel and after expansion into the large vessel, the equilibrium is almost fully achieved even in worst case. Other disturbing effects were also investigated in detail. The uncertainty budget of the generated calibration pressures (2@sigma@-level) gives a total uncertainty below 0.1% in the pressure range 0.1-to- 10 mbar (single step expansion) and below 0.15% in the pressure range 0.001 to 0.1 mbar (two step expansion).

10:20am **VST-ThM7 Transfer Standard for Low Rates of Gas Flow*, R.F. Berg,*** National Institute of Standards and Technology

We describe an improved laminar flow meter suitable for comparing gas flow rates from 1 -to- 1000 micromol/s (about 1 to 1000 sccm) with an accuracy of approximately 0.1%. The flow impedance consists of coils of commercial quartz capillary tubing. The capillary radius is less than 0.01% of the length, which reduces corrections due to gas expansion and the pressure drop at the entrance. A small aspect ratio also was used in the flow meter recently modeled by Berg and Tison.@footnote 1@ That flow meter's impedance was a machined helical duct of rectangular cross section. In contrast, the present quartz capillaries have a circular cross section, which allows the model of the flow meter to use Van Dyke's analytical expression for centrifugal effects.@footnote 2@ Although such corrections are as large as 3% at the largest flow rates, the model requires only one free parameter, the capillary radius. A model with minimal empiricism allows the standard to be used confidently with varied gases, varied outlet pressures, and integrated measurements as well as continuous measurements. Measurements with two primary standards are described. The first set compared the transfer standard's continuous output to PVT measurements, and the second set compared the integrated output to the mass changes of a gas cylinder. @FootnoteText@ @footnote 1@ AIChE J. 47, 263 (2001). @footnote 2@ J. Fluid Mech. 86, 129 (1979).

10:40am **VST-ThM8 Overview of Two CCM Key Comparisons in Low Pressure (1 Pa - 1000 Pa) - How Good are MEMS Sensors as Transfer Standards?*, A.P. Miiller,*** National Institute of Standards and Technology

This talk will provide an overview of two recent CCM key comparisons of primary pressure standards operating in the range 1 Pa to 1000 Pa at eight National Metrology Institutes (NMIs). The objective of the two comparisons, one in absolute pressure the other in differential pressure at a nominal line pressure of 100 kPa, was to determine the degrees of equivalence of the measurement standards. An earlier comprehensive study@footnote 1@ of low-pressure transducers showed that no one type of transducer could meet all requirements for the transfer standard. Consequently the transfer standard package was constructed using four high-precision pressure transducers, two capacitance diaphragm gauges to provide high resolution at low pressures and two (MEMS) resonant silicon gauges to provide calibration stability. Two nominally identical transfer packages were used to reduce the time required for the measurements, with Package A being circulated among laboratories in the European region (IMGC, NPL-UK, and PTB) and Package B being circulated among laboratories in the Asia-Pacific region (CSIRO, KRISS, MSL-NZ, and NPL-I). The results obtained with different transfer packages were normalized by using data obtained from simultaneous calibrations of the two packages at the pilot laboratory (NIST). The degrees of equivalence of the measurement standards were determined in two ways, deviations from key comparison reference values (KCRVs) and pairwise differences between these deviations. Apart from a few results identified as outliers, the measurement standards were generally found to be equivalent relative to the KCRVs, though some additional instances of nonequivalence were observed between given pairs of standards. The results revealed no significant relative bias between different measurement methods used by the NMIs to realize their standards. @FootnoteText@@footnote 1@ Miiller A. P., "Measurement performance of high-accuracy low-pressure transducers", Metrologia, 1999, 36 (6), 617-621.

11:00am **VST-ThM9 Some Consideration About Uncertainty on the Primary Vacuum Measurements*, A. Calcatelli,*** *M. Bergoglio,* Consiglio Nazionale delle Ricerche, Italy

The need of better characterisation of high quality gauges in the various vacuum ranges represents a considerable input to accurate analyses of the available primary systems. That was connected to the need of defining ranges and related uncertainties for the international comparisons. The uncertainties of the IMGC systems are discussed. Static system: the measurand, p@subi@,is given by p@subi@=p@sub0i@R@subj@T@subV@/T@subv@ where the quantities p@sub0i@, T@subv@, T@subV@ and R@subj@ represent respectively inlet pressure values, the temperatures of the involved volumes and the expansion ratio between the considered volumes. These quantities are generated by several other factors. The input quantities for R@subj@ are correlated since the method is based on the accumulation of the gas inside one of the involved volumes and consequently on sequential measurements of set of pressures. In turn R@subj@ is correlated to p@sub0i@. The covariance matrix is taken into account for the evaluation of the final p@subi@ uncertainty. Dynamic system: the measurand, p@subi@, is given by p@subi@=(Q@subi@/S@subeff@)F@subci@ where the quantities Q@subi@, S@subeff@, F@subci@ represent the values of the gas-flow-rate at pressure p@sub i@, the effective pumping speed at conductance level and the temperature correction factor. These factors are related to several other input quantities. S@subeff@(C/(1+C/S@subp@) is a function of the conductance C and of the pumping speed through the ratio C/S@subp@. C is modelled mathematically and C/S@subp@ is measured in a separated experiment and is periodically checked. Q@subi@ is generated and measured at each desired pressure p@subi@ in the calibration chamber and depends on several quantities. F@subc@, related to the temperatures in the calibration chamber and in the flow-meter is also measured at each pressure level. The uncertainty of both the systems is discussed taking into account the possible correlation among all the considered quantities.

11:20am **VST-ThM10 Performance Test of Vacuum Components and System*, K.H. Chung,*** Korea Research Institute for Standards and Science, South Korea **INVITED**

KRISS has established vacuum standards from atmospheric pressure down to ultra high vacuum of 5 x 10-7 Pa, and the leak standards in the range of 5.0 x 10-5 ~ 6.0 x 10-7 Pa-m@super 3@/s. The Ultra High Vacuum standards in the range of 5x10-7 ~ 10-3 Pa with a relative uncertainty of 2x10-2 is maintained by dynamic flow method using porous plug technique, and the High Vacuum 10-3 ~ 10-1 Pa with an uncertainty of 5 x 10-3 by dynamic flow method, and Low Vacuum 10-1 ~ 105 Pa by Ultrasonic Interferometer Manometer with an uncertainty of 10-2 ~ 10-5. Now, KRISS is developing a medium vacuum standards by volume expansion method. The market for vacuum equipments in Korea is very big since we have big semi-conductor manufacturers. But most of the vacuum equipments are imported, for our vacuum industry is very weak in technology and very small in size. We circulated Enquetes to the vacuum users, industry, universities, and research institutes, to find out why the Korean industry avoid buying Korean Vacuum products, and most people replied that the lack of reliability and credibility of our products is the most serious problem besides financial difficulties. In order to improve this situation, The Center for Vacuum Technolgy has been established in KRISS. In Center for Vacuum Technology, the integrated comprehensive test and evaluation facilities for vacuum system will be set up and certify the quality and specifications of wide ranges of vacuum gauges and mass flow controllers, all kinds of vacuum pumps, components, vacuum properties such as outgassing, thermal desorption spectroscopy and permeation and diagnostics of plasma in the system. The total testing items are 72 and number of systems is 17. The project has started in October 1999, and will continue to October 2003.

Applied Surface Analysis
Room 134 - Session AS-ThA
Adhesion and Corrosion

Moderators: M.-L. Abel, University of Surrey, UK, J.F. Watts, University of Surrey, UK

2:00pm **AS-ThA1 Substrate Preparation and Stud Pull Adhesion of Metal Films on Graphite-Epoxy Composites*, P. Kraatz,*** Technical Consulting Services*; W. Mellberg,* Lockheed Martin*; G.L. Young,* San Jose State University

Sputtered multilayers of chromium and copper are employed as adhesion enhancing layers on surfaces of graphite-epoxy substrates. These sputtered layers provide a basis for electroplating copper and silver. The effects of substrate preparation techniques upon adhesion strength of deposited metal films are investigated. The stud pull adhesion test is employed as a tool for quantitative measurement of adhesion strengths of metal films on graphite-epoxy substrates. Preparation techniques studied include wet or dry abrasion, using "Scotch Brite" or 400 grit sandpaper, and non-abrasive cleaning, using surfactants, water, and solvents. For as-sputtered material, highest stud pull strengths are associated with wet abrasion and pre-sputter cleaning with aqueous surfactants, DI water, and solvents. Lowest adhesion strengths are associated with non-abrasive cleaning, using the same agents. Effects of thermal cycling in air upon adhesion vary with surface preparation before sputtering. Dry abrasion and solvent cleaning lead to the highest adhesion strengths after thermal cycling, while non-abrasive cleaning is again associated with the lowest strengths. Adhesion of electroplated silver and copper to sputter coated graphite-epoxy also varies with surface preparation before sputtering. In contrast to as-sputtered results, abraded surfaces are associated with reduced plating adhesion, and unabraded surfaces with enhanced plating adhesion. Surface analysis (AES and ESCA) results suggest that formation of a thin carbide phase at the interface between the graphite-epoxy and sputtered chromium correlates with higher adhesion strength, while unusually high oxygen content at the interface correlates with lower adhesion strength.

2:20pm **AS-ThA2 Polymer-metal Interfaces: The Influence of a Metallic Surface on the Interphase Formation Mechanisms*, A.A. Roche,*** INSA de Lyon, France*; M.-G. Barthés-Labrousse,* CNRS, France*; J. Bouchet,* INSA de Lyon, France*; F. Debontridder,* CNRS, France

Epoxy-diamine networks are extensively used as adhesives or paints in many industrial applications. It will be shown in this paper that studies carried out starting from the adsorption of simple diamine molecules to the application of an epoxy-diamine mixture onto oxidized metallic surfaces can lead to a better understanding of the chemistry inducing the interphase formation and to the adhesion mechanisms of epoxy systems on metallic substrates. Results obtained following deposition of either pure diamines or mixtures of epoxy and diamines onto gold and aluminum surfaces will be presented. When mixtures of epoxy-diamine are applied onto gold coated substrates, the properties obtained for the coating are the same as the bulk network ones. When the precursors are applied on oxidized or hydroxylated metallic substrates and subsequently cured, an interphase is created between the substrate and the polymer, which has chemical, physical and mechanical properties quite different from the bulk polymer ones. For example, when mixtures of epoxy-diamine are applied onto aluminum surfaces, the glass transition temperature, the reaction rate between amine and epoxy, the interphase thickness, the residual stresses within the interphase and the Young's modulus of the interphase all depend on the amine nature (aromatic, aliphatic or cycloaliphatic), the stoichiometric ratio, the processing conditions (time and temperature), the organic layer thicknesses and the metallic surface treatment nature. Characterization of the metallic surfaces (XPS, IRRAS, GXRD) shows that, whatever may be the surface treatment of the metallic substrates, adsorption of the diamine monomer onto the metallic hydroxylated surface leads to both Lewis (bonding between the metallic surface cationic sites and the diamine nitrogen atom) and Brønsted (bonding between the hydroxyl groups and protonated amine function) acid-base interactions. The change in the ratio between Brønsted and Lewis type interactions can be ascribed to the differences in hydroxylation of the superficial oxide layer. Besides, coating spectroscopy data (FTIR, FTNIR, DSC, DMTA, H+ and C13 NMR, SEC, ICP and POM) suggest that diamine monomers dissolve the metallic hydroxylated oxide layer. Then, the metallic ions diffuse through the liquid organic layer to form a complex by coordination with diamine monomers (chelate or ligand). When metal-amine complexes are mixed within the DGEBA monomer a phase separation is induced during the curing cycle, leading to the formation of a new network. Furthermore, when the organo-metallic complex concentration is higher than the solubility product, these complexes crystallize as sharp needles. They align themselves parallel to the metallic oxidized surface and act as oriented short fibers in an organic matrix thus leading to an increase of its mechanical properties.

2:40pm **AS-ThA3 Acid-base Characterisation of Metallic Surfaces*, M.-G. Barthés-Labrousse,*** CNRS, France **INVITED**

3:20pm **AS-ThA5 Effects of Plasma Treatment on Solder Resist Investigated by Contact Angle, XPS and AFM**, *F.L. Hall,* Micron Technology Inc.*; **C.A. Bradbury**,* Micron Technology Inc., US

During the initial development of the chip on board (COB) fine ball grid array (FBGA) process, repeated reliability failures resulting from delamination between the epoxy molding compound and the solder resist interface created a need to investigate treatments to improve adhesion between these surfaces. One such means for improvement was exposing the solder resist to plasma prior to molding. A study of the effects of plasma treatment on solder resist as it applies to the assembly of COB FBGA packages was performed. In this study, solder resist samples were subjected to direct and downstream plasma treatments at various settings. The treated samples were then examined for chemical and physical changes via X-ray Photoelectron Spectroscopy (XPS), Atomic Force Microscopy (AFM) and contact angle. Changes in the surface during storage were also evaluated.

3:40pm **AS-ThA6 Correlation between Surface Topography and Corrosion Rate: An Investigation by Scanning Force Microscopy*, J.E. Castle,*** *P.A. Zhdan, P. Singjai, T. Simpson,* University of Surrey, U.K.

In the course of our work with many metals, alloys and inorganic materials in media of differing levels of aggression we have found an interesting broad correlation between surface topography and the extent of aqueous corrosion. The correlation is particularly apparent when use is made of scanning force microscopy (SFM) to monitor surface roughness under conditions in which the extent of corrosion can be measured by an independent method - such as solution analysis. This enables corrosion rates to be inferred from in-situ or ex-situ measurements of surface topography, made by SFM, in media or with surfaces that are not amenable to normal means of corrosion rate measurement. We draw attention to this correlation using several examples, such as etching of copper, corrosion of duplex steel and ferritic steel in hydrochloric acid, or the corrosion of brass in aerated water, and corrosion of pottery glaze in alkaline wash, which have been chosen to illustrate the phenomenon in both etching and in oxidising conditions. Underlying reasons for the correlation are discussed and it is shown that a useful outcome of the work is that it permits measurements by in situ SFM to be used for interpolation or extrapolation of data obtained by electrochemical methods or by analysis of the corrodent solutions. The SFM as an instrument is becoming widely available and this method of measurement thus has a wide application. It is suggested that as more robust forms of the SFM instrument become available, there is the possibility of using this technique as a corrosion monitor under circumstances in which measurement of corrosion rate is difficult by more conventional methods.

4:00pm **AS-ThA7 Corrosion Studies Using X-Ray Techniques*, H.S. Isaacs,*** Brookhaven National Laboratory **INVITED**

A major advantage of x-ray techniques is that they allow in situ studies of the processes taking place. A range of applications of synchrotron x-rays for the study corrosion will be briefly reviewed. These include novel atmospheric measurements using ionize air to determine Volta potentials usually made using Kelvin probes, and scanning x-ray fluorescence techniques for the analysis of corrosion products at the corroding interface and within solution. Emphasis will be given to the measurement of passive oxide films. These are a few nanometers thick and responsible for corrosion resistance. Examples using x-ray absorption will be given of the chemistry of passive oxide films on iron and stainless steels, their electrochemical formation, dissolution, and the behavior of chromium, the critical additive to stainless steels.

4:40pm **AS-ThA9 The Physical and Chemical Surface Structure of Iron Exposed to Carbon Tetrachloride-Saturated Water*, D.J. Gaspar,*** *A.S. Lea, M.H. Engelhard, D.R. Baer,* Pacific Northwest National Laboratory*; R. Miehr, P.G. Tratnyek,* Oregon Graduate Institute

The corrosion of metallic iron by carbon tetrachloride (CCl@sub 4@) has been studied by surface analysis techniques, including time-of-flight secondary ion mass spectrometry (TOF-SIMS), Auger electron spectroscopy

(AES), and x-ray photoelectron spectroscopy (XPS). Permeable barriers made of "zero-valent" iron powders are among the methods being considered to assist environmental remediation by catalytic destruction of halogenated solvents. Understanding the chemical and physical properties of the corrosion layer formed on the iron particles is critical in the design of advanced catalysts for environmental remediation because the oxidized layer on the surface of the metallic iron particles is modified during reduction of the halogen-containing species. Among the specific questions is the nature of "active" sites that may facilitate the reduction of the halogenated hydrocarbons. To this end, selected polycrystalline zero-valent iron particles were treated with CCl@sub 4@-saturated water for a period of 1-7 days, and the physical and chemical structure of the surface was studied. The chemical and physical structure of the oxidized iron surface was then examined, revealing localization of chloride within etch pits.

5:00pm **AS-ThA10 Adsorption of Organic Acids onto the Surface of 2024-T3 Aluminium Alloy: The Role of Intermetallic Particles***, **A.J. Roberts**,* Kratos Analytical Ltd., UK*; D. Engleberg, Y. Liu, G.E. Thompson, M.R. Alexander,* UMIST, UK

Self-assembled monolayers of alkyl-phosphonic and carboxylic acids have been proposed as alternatives to conventional chrome-based pre-treatments for corrosion protection of aluminium. These organic pre-treatments aim to form coupling layers between the air-formed aluminium surface and the resin component of paints and adhesives.@footnote 1@ Commercial aluminium alloys contain intermetallic particles which mechanical and chemical finishing processes may expose at the surface.@footnote 2@ Analysis is complicated by the size of the particles that can range from 0.1-10µm. Auger analysis has suggested preferential adsorption of long chain phosphonic acids at iron-containing inclusions in an AlMg1 alloy, although no chemical state or quantitative information was presented.@footnote 3@ Small area and imaging XPS, with a Kratos Axis Ultra spectrometer, has been used to obtain quantitative elemental and chemical state information from such particles (Al@sub 2@Cu and Al@sub 2@CuMg) at the mechanically polished surface of Al 2024-T3, an alloy of importance in the aerospace industry. Alkyl-phosphonic and -carboxylic acids were adsorbed from dilute solutions allowing comparison of coverage and chemical state between the second phase intermetallics and the hydrated alumina surface of the matrix. Comparison is also made with the adsorption characteristics on super pure Al.@footnote 4@ Polarisation modulation IRRAS provides complimentary information on the interfacial bonding and degree of order within the monolayers. @FootnoteText@ @footnote 1@I Maege et al. Macromol. Symp. 126 (1997) 7.@footnote 2@I Pires et al. Transactions of the Institute of Metal Finishing 78 (2000) 179. @footnote 3@Ch. Bram et al. Fresenius J Anal Chem 358 (1997) 108. @footnote 4@ TA Lewington et al. Comparison of alkyl-carboxylic and phosphonic acid monolayer formation on Al, in preparation for submission to Surf. Interface Anal.

Biomaterials
Room 102 - Session BI-ThA

Cell-Surface Interaction

Moderator: G.J. Leggett, UMIST, UK

2:40pm **BI-ThA3 Developmental Studies of Electrical Activity of Artificially Constructed Neuronal Cell Networks***, **C.D. James**, A.J. Spence, H.G. Craighead, M.S. Isaacson,* Cornell University*; N. Dowell, W. Shain, J. Turner,* Wadsworth Center

The hippocampus has been implicated in a range of brain functions such as the internal representation of space and memory consolidation. Dissociated hippocampal pyramidal cell cultures have yielded vital information about single unit and small network electrophysiology, yet monitoring synaptogenesis and the development of electrical activity within cell networks has proved to be a difficult task. The construction of neuronal cell networks has been investigated by many researchers for this purpose, and our labs have utilized microcontact printing and microfabricated electrode arrays to construct and study cell networks. Selective spatial organization of proteins and molecules have been used to direct neuronal cell attachment and neurite outgrowth in vitro, while microelectrode arrays allow long-term, non-invasive studies on developing network populations. The combination of both technologies has allowed our labs to monitor field and action potentials of designed cell networks in order to investigate the relevance of such factors as cell morphology and neuron-substrate interaction on the development and stability of connected units. Multi- and single-unit extracellular potentials of 50 to 300 microvolts have been observed and recorded with five simultaneous channels to enable single unit discrimination. Whole cell recordings were also performed to provide guidance in isolating single units in our extracellular recordings, while immunochemical staining of networks for synaptic proteins such as synaptophysin and PSD-95 was used to identify putative synapses. We believe that such studies may be able to provide valuable information about the maturation of coordinated activity between cells, primarily in regards to the influence of neuron morphology on action potential invasion into the somato-dendritic regions of firing cells, as well as on the developmental segregation and distribution within cells of relevant molecules such as ion channels and synaptic proteins.

3:00pm **BI-ThA4 The Affects of Geometric Constraints on Neuronal Process Extension***, **A.M.P. Turner**, S.W.P. Turner, R. Terao, H.G. Craighead,* Cornell University*; N. Dowell, W. Shain,* NYS DOH Wadsworth Center*; G. Withers, G. Banker,* Oregon Health Sciences University

Our research has involved the study of how central nervous system (CNS) cells attach to and grow on surfaces topographically modified with micrometer-sized features. In particular, we have studied the growth of rat hippocampal neurons on surfaces patterned with pillars. Patterned silicon substrates were made using conventional semiconductor methods and polymer embossing techniques were used to make transparent substrates. It was observed that the geometric constraints to which a neuron is exposed have a significant impact on various aspects of neuronal process development, including the rate of neurite (dendritic and axonal) outgrowth, neurite morphology, dendritic branching, and specific protein production, transport and organization. Fluorescence, scanning electron, and phase-contrast time-lapse microscopies were used to analyze and quantify the growth of neurons on surfaces with 1 to 2 µm tall pillars of various widths, 500 nm to 2 µm, and inter-pillar spacings, 1.0 µm to 5 µm. We observed a 50 percent increase in the rate of neurite outgrowth on surfaces with pillars versus smooth surfaces. It was also observed that in arrays with spacings less than 2 µm, the majority of neurites grow along 90 and 45 degree paths from the soma whereas with spacings of 4 µm and greater, neurites revert back to morphologies observed on smooth surfaces. Dendritic branching was found to increase with a decrease in inter-pillar spacing and immunochemical staining demonstrated various correlations between protein organization and pillar locations. The goal of these studies is to learn more about the fundamental interactions between CNS cells and surface structure.

3:20pm **BI-ThA5 The Use of Surface Composition to Control Cell Phenotype Expression***, **J.J. Hickman**, P. Molnar, G. Jacob, M. Das, T. Tauber,* Clemson University

There is currently a large amount of interest in neuronal STEM cell manipulation to create stable phenotypes. The initial phase of CNS development is characterized by the proliferation of the precursor cells, followed by the generation of neurons and glia. The neurons are differentiated into different neurotransmitter phenotypes as well as glial cells. However, the factors that control the differentiation of the precursor cells into differentiated cell types are still mainly unknown. It is believed that the cell environment plays a key role in the specification of neuronal cells, even though a cell intrinsic developmental program is important in regulating cell lineage. We have shown it may be possible to manipulate the development of specific phenotypes through cell-surface interactions. In the present study, the expression of neuronal cell phenotype was examined in a defined in vitro system in which embryonic rat cortical cells were grown on silica substrates modified with artificial surfaces composed of silane self-assembled monolayers (SAMs) in serum-free medium. Experiments were conducted utilizing various neurotrophic factors and various substrates to examine cortical neuron phenotype expression. Cultures were immunostained with a panel of antibodies to detect specific differentiation markers. On poly-D-lysine and DETA, glutamatergic cells represented 30-40% of total cells and GABAergic cells represented about 50-60% of total cells, which is consistent with immunocytochemical findings in vivo. On 13F the ratio of glutamatergic to GABAergic was greater. We will present these results as well as an explaination for the observed effects.

3:40pm **BI-ThA6 Stretching and Fibroblast Growth on GRGDSP-Peptide Modified Silicone Membranes***, L. Hanley, **S.S. Lateef**, S. Boateng, T.J. Hartman, C. Crot, B. Russell,* University of Illinois at Chicago

Diseased, hypertrophic human heart muscle cells (cardiac myocytes) are found to increase in length and volume due to excessive mechanical load. We are developing an entirely new cell culture in silicone elastomer that will mimic the in-vivo cell phenotype to address such questions in cardiac mechanobiology. We chemically modify silicone membranes to improve their ability to culture cardiac myocytes under dynamic stretching, thereby allowing study of mechanical effects. It is well known from studies of cellular attachment that several intrinsic proteins found on the cell surface will recognize and attach to the GRGDSP peptide sequence. We plasma oxidize the surface of the silicone membrane; functionalize it with amine via reaction with 3-aminopropyltriethoxysilane; attach a sulfo-maleimide cross-linker; then attach a 15-residue peptide, acetyl-CGGEGYGEGRGDSPG-amide, to the cross-linker through its terminal thiol group. The membranes are characterized by x-ray photoelectron spectroscopy, spectochemical analysis, and radiolabelling. Stretching studies with radiolabelled cysteine (in place of peptide) show that the modified layer survives on the surface for 48 hours of stretching in cell culture media. The GRGDSP peptide bound silicone shows enhanced binding of rat fibroblasts when compared with amine-functionalized and unmodified silicone surfaces.

4:00pm **BI-ThA7 Surface Characterization and HCAEC Adhesion Studies of IPN Modified 316 L Stainless Steel**, ***G.M. Harbers,*** Northwestern University; *T.A. Barber, M.E. Yanez, H.B. Larman,* University of California, Berkeley; *K.E. Healy,* University of California, Berkeley, U.S.A

Interactions between synthetic biomaterials and components of the cardiovascular system still remain poorly understood. In particular, the process of restenosis following intravascular stent deployment remains a significant problem. Coatings that minimize protein adsorption and monocyte adhesion and proliferation may reduce late-term in-stent restenosis and prevent secondary interventions. In this work, a previously developed non-fouling P(AAm-co-EG/AA) interpenetrating polymer network (IPN) was applied to clinically relevant cardiovascular stent material (316L SS). The transfer of the technology from previous substrates (quartz, TiO@sub 2@/Ti, polystyrene) to SS was confirmed using water contact angle goniometry, XPS, and cell-material interactions. Water contact angle data was similar to what was previously reported for quartz substrates and XPS confirmed the addition of each subsequent layer. To test the ability of the modified material to resist cell adhesion, substrates were seeded with primary human coronary artery endothelial cells (HCAECs). Following a 24h incubation, cells were labeled and examined using fluorescent microscopy. HCAECs adhered to both the unmodified SS and the positive control (TCPS) but not to the IPN modified material (TCPS>SS>>IPN~PEG(NH@sub 2@)@sub 2@; 8875±2128, 6972±721, 124±22, and 99±29 cells/cm@super 2@ on respective surfaces). Cells on unmodified SS coupons had a similar morphology to those seeded onto TCPS. However, the few viable cells that attached to the IPN and PEG(NH@sub 2@)@sub 2@ remained spherical and non-spread. It has been proposed that endothelialization of the stent surface can improve stent performance by creating a native tissue layer. Therefore, since the IPN/316L SS system is amenable to peptide modification, the identification of endothelial cell specific peptides to promote preferential endothelial cell adhesion, migration, and proliferation is under investigation.

4:20pm **BI-ThA8 Improved Functionalization for Chemically Patterned Polystyrene Surfaces**, *A.A. Meyer-Plath,* ***K. Schröder,*** *A. Ohl,* Institute of Non-thermal Plasma Physics, Germany

Tight contact between living cells and polymeric materials is a key characteristic of implant materials, medical, pharmaceutical diagnostic devices, and in vitro cell culturing. To improve cell adhesion and growth, surface modification is required for almost all types of polymer. Plasma-chemically introduced functional groups are widely used for this purpose. Type and density of surface functionalities control adsorption behaviour of cell-signaling molecules. Also, selective immobilization of biologically active molecules (e.g. attachment factors) is possible. This way, the polymer surface provokes cell responses. Chemical patterns for different cellular responses are the basis for some advanced applications of biomaterials. They may directly induce selective cell adhesion. Plasma functionalization is the basis for pattern generation. Here, continuous wave and pulsed microwave and radio frequency plasmas in nitrogen-containing gas mixtures were studied for grafting of nitrogen functional groups on polystyrene. Plasma conditions were optimized in two respects: either to obtain a high selectivity for amino groups, or to maximize the overall density of nitrogen groups. The obtained functionalized surfaces were investigated by means of XPS, contact angles and cell culture. Specific plasma conditions lead to surfaces with high-density cultures of adherent cells after 24 hours of culturing, exceeding significantly densities on the untreated or oxygen-plasma-treated polymer. The highest level of nitrogen and amino functionalization was obtained using pulsed microwave plasmas. Patterning of the chemical functionalization was realized by a hydrogen plasma treatment using a laser-cut metal mask. The chemical pattern was verified by XPS with high local resolution.

4:40pm **BI-ThA9 Controlled Cell Adhesion on Honeycomb Films of Biodegradable Polymers**, ***T. Nishikawa,*** RIKEN Frontier Research System, Japan; *K. Nishikawa, R. Ookura, J. Nishida,* Hokkaido University, Japan; *K. Arai, J. Hayashi,* RIKEN Frontier Research System, Japan; *M. Matsushita, S. Todo,* Hokkaido University, Japan; *M. Hara, M. Shimomura,* RIKEN Frontier Research System, Japan

We report that a honeycomb like micro-porous film (honeycomb film) can control cell adhesion of hepatocytes and cardiac myocytes. The honeycomb films were fabricated by casting a dilute solution containing biodegradable polymers (poly-L-lactic acid (PLLA) and poly-@epsilon@-caprolactone (PCL)) and an amphiphilic polymer on water surface in a humid atmosphere. By the method, self-supported honeycomb films were obtained. Hepatocytes were cultured on a self-supported honeycomb film of PLLA. The cells formed a single layer of columnar shape cells with a thickness of 20 µm. The tissue formation of hepatocytes specifically occurred on the honeycomb films of PLLA, but not on flat films of PLLA. The artificial tissue of hepatocyets expressed high level of albumin secretion, which was comparable to that of spheroids of hepatocytes. Furthermore we succeeded in three dimensional culturing of hepatocytes. Hepatocytes formed two single layers on each sides of a self-supported honeycomb film of PLLA. Honeycomb film of PCL was stretched out uniaxially by mechanical force. The honeycomb pores were deformed into elongated hexagons and rectangles. Since the array of the elongated hexagons is anisotropic, the stretched honeycomb film is applicable to guiding cell alignment. We used a stretched honeycomb film of PCL as a cell culture substrate for cardiac myocytes. The substrate was fabricated by placing a stretched honeycomb film of PCL onto a glass plate. Cardiac myocytes of rat embryo were not aligned in a specific direction on regular honeycomb patterned surface. On the other hand, cardiac myocytes were aligned along the long axis of the stretched micro-pores on the stretched honeycomb film. Thus the honeycomb films can control cell alignment as well as cell attachment. Based on the results, we expect that the honeycomb films can be designed, fabricated, and utilized in accordance with target tissues.

5:00pm **BI-ThA10 New Substrates for Retinal Cell Transplantation**, ***C.J. Lee,*** *S.F. Bent, P. Huie, M. Blumenkranz, H. Fishman,* Stanford University

A novel treatment for age related macular degeneration (AMD) is currently being investigated. This treatment involves the transplantation of human pigment epithelial cells (PE) on a carrier substrate to rescue the diseased retina. Various substrates including synthetic biodegradable polymers and biocompatible substances have been proposed as carrier substrates. Biocompatible materials offer the ability to coexist in the subretinal space, thus reducing immune rejection. The goal of this work was to grow cells on various biocompatible materials and to show the survival and longevity of the cells. Without specific constraints, the cells exhibit a variety of morphologies, including cuboidal and elliptical structures. In this study, surface modifications were employed to control the growth and morphologies of the cells. The cells have been successfully grown on these modified substrates, exhibiting stable function for at least two weeks in culture. In summary, we show that engineering biocompatible substrates is possible and that stable growth of cells occurs. The possibility of the feasibility of this treatment in animals will be discussed.

Electronics

Room 124 - Session EL-ThA

In-Situ Semiconductor Characterization

Moderator: D.E. Aspnes, North Carolina State University

2:00pm **EL-ThA1 In-situ Analysis, Monitoring and Control of III-V-Semiconductor Epitaxial Growth**, ***W. Richter,*** TU Berlin, Germany **INVITED**

Epitaxial growth of semiconductor structures requires control of the growth process on the atomic scale. This, however, is difficult to achieve by just controlling macroscopic growth parameters like partial pressures (fluxes) and temperatures. It is thus desirable to have in real time microscopic information from the growing surface for a direct analysis and conseqently control on the ongoing growth process. Optical probes offer in this respect important advantages: they are in general non invasive, they can be fast in obtaining the needed information and finally they can be applied in all growth environments (vacuum or gasphase based growth methods). The "optical" disadvantage of having a low spatial resolution can be overcome quite often by extra "calibration" measurements with high resolution spatial probes like STM, AFM, LEED. I will discuss first the analysis of reconstructed surfaces by reflectance anisotropy (RAS). Simultaneous measurements in MBE and MOVPE together with theoretical calculations allow to correlate optical spectra with surface reconstructions. Based on these basic data it is possible to describe adsorption and desorption processes of the basic constituents (Group III and V elements). Moreover, growth in dependence of partial pressure and temperature can be described via different modes in a flux - temperature phase diagram, allowing thus to define the surface growth status nearly independent of the special epitaxial equipment. Monitoring and control of device growth seem to be now possible.

2:40pm **EL-ThA3 Direct Numerical Inversion of Real-time Ellipsometric Data for Monitoring and Control of Optical Filter Deposition***, D. Kouznetsov, A. Hofrichter,* ***B. Drevillon,*** Ecole Polytechnique CNRS, France

In situ ellipsometry is well known to be one of the most sensitive, non-disturbing tools for controlling and monitoring the growth of thin films. However the rapid advances in ellipsometric instrumentation, especially the increasing real time spectroscopic capabilities of state of art ellipsometers necessitate the development of new algorithms for an optimal assessment of the available information. In this work we apply a new direct numerical inversion algorithm for the real-time reconstruction of homogeneous and inhomogeneous refractive index profiles for the monitoring and the control of optical thin film depositions. The algorithm is based on a second order Taylor decomposition of the coefficients of the Abeles matrices of the newly grown layer. The variation of the real-time spectroscopic ellipsometry data are expressed as polynomial functions depending on the dielectric constant and the thickness of the newly grown layer. This allows a direct inversion of the ellipsometric signal and assures the high speed of the algorithm. Typical inversion times are 150 ms for 16 wavelength with a typical precision of 0.02 for the refractive index and less than 2% error in the reconstructed thickness. The algorithm is successfully applied for the real-time material characterization of transparent and weakly absorbant silicon oxynitrides deposited by plasma enhanced chemical vapor deposition. The complete process space can thus be explored in one single run. Combined with traditional ellipsometric control algorithm this method allows to grow multilayer and gradient optical coatings with high accuracy in respect to initial design.

3:00pm **EL-ThA4 Integrated Multiwavelength Parallel-processing Rotating-compensator Ellipsometer/Reflectance-difference Spectrometer for Real-time Measurement and Control of OMCVD Growth***,* ***K. Flock****, M. Ebert, K.A. Bell, D.E. Aspnes,* North Carolina State University

Previous research has underlined the importance of real-time diagnostics for epitaxial growth of semiconductor materials and structures. We describe an optical system integrated with a modified rotating-sample commercial organometallic chemical vapor deposition (OMCVD) reactor that combines the functions of spectroscopic ellipsometry (SE) and reflectance-difference spectroscopy (RDS) in a single optical path to return information about growth rates, compositions, and film thicknesses (SE) and surface chemistry (RDS). The system is essentially a rotating-compensator ellipsometer for increased diagnostic power relative to rotating-polarizer or rotating-analyzer designs, with the rotation rate of the compensator synchronized to that of the sample. Synchronization reduces noise in the SE data by eliminating random optical-anisotropy contributions and also allows us to measure the non-normal-incidence RD spectrum directly. The original sample spindle was replaced with a design that allows sample runout to be adjusted dynamically to provide additional improvements in signal-to-noise ratios. A 1024-element photodiode array detector with a 0.2 m spectrograph provides a spectral range of 240 to 840 nm. Software designed to optimize both real-time response and repetition rate permits complete spectra to be obtained at a 6 Hz rate with a 400 MHz computer. Using a prototype rotating-polarizer system we demonstrated sample-driven closed-loop feedback control of a graded-composition InGaP structure grown on GaAs, where the composition was varied parabolically with thickness. During the growth of this structure it was necessary to reduce the flow through the trimethylindium by about half, which the RD data indicate is due to a change of incorporation efficiency due to an observed change of surface reconstruction.

3:20pm **EL-ThA5 In-situ Monitoring of Ag Film Growth on Si(111)7x7 Surface by Optical Second Harmonic Generation***,* ***H. Hirayama****, T. Kawata, K. Takayanagi,* Tokyo Institute of Technology, Japan

A growth of Ag films on the Si(111)7x7 surface was monitored by optical second harmonic generation (SHG). Ag-coverage dependent intensity oscillation was observed in p-polarized SHG signals with 1.20,1.30 and 1.40 eV pump photon energy. As has been reported recently by Pedersen et al, the SHG intensity oscillated with the Ag coverage. However, on the contrary to the previous report, the first peak in the oscillations was observed at 3ML for all the pump energy. The peak position was independent on the pump energy. Meanwhile, the subsequent peaks shifted toward lower coverage with the increase in the pump photon energy. A detailed comparison of the SHG intensity and AFM images of the Ag film grown on the Si(111) substrate showed that many three-dimensional Ag islands nucleated at the coverage for the first peak. The surface morphology changed to be two-dimensional smooth one at the coverage for the subsequent peaks. The AFM images and the SHG spectrum taken at the coverages of the peaks showed that the first peak in the SHG intensity oscillation corresponded to the local plasmon resonance with the 3D Ag island formation. The subsequent peaks were caused by the transitions with the quantized electronic states confined in the thin, flat Ag films. The characteristic transitions between the electronic states localized at the Ag/Si(111)7x7, 1x1 and @sr@3x@sr@3 interfaces were also detected as resonant peaks in the s-polarized SHG spectrum with the excitation photon energy ranged from 1.05 to 1.70eV.

4:00pm **EL-ThA7 RHEED Intensity Oscillation during Thermal Oxidation on Si(001) Surface with O@sub 2@***,* ***Y. Takakuwa****, F. Ishida,* Tohoku University, Japan

Auger electron spectroscopy combined with reflection high energy electron diffraction (RHEED-AES) was applied to investigate the surface reaction dynamics during thermal oxidation on Si(001)2x1 surface with O@sub 2@. In the RHEED-AES measurement, O KLL Auger electrons excited by a grazing-incident electron beam for RHEED observation were detected, enabling to observe simultaneously the SiO@sub 2@ coverage and surface morphology. In the temperature region of two-dimensional growth of SiO@sub 2@ islands at 630~800°C as confirmed by the time evolution of O KLL Auger electron intensity, an oscillatory behavior in RHEED half-order spot intensity was observed, indicating that etching of the surface occured between SiO@sub 2@ islands. The etching rate obtained by the oscillation period was 0.039 ML/s at an O@sub 2@ pressure of 2x10@super -7@ Torr independently of the temperature and SiO@sub 2@ coverage, and increased in proportion to the O@sub 2@ pressure, suggesting that the etching reaction was rate-limited by O@sub 2@ supply. Since part of adsorbed oxygen atoms is consumed for nucleation and two-dimensional growth of SiO@sub 2@ islands in this temperature region, the assigned rate-limiting reaction means that the etching reaction takes place not only through SiO desorption but also through SiO@sub 2@ growth, that is, incorporation of Si atoms into SiO@sub 2@ islands. The fraction of the amount of incorporated Si atoms into SiO@sub 2@ islands to that of etched Si atoms will be discussed against SiO@sub 2@ coverage.

5:00pm **EL-ThA10 SR-TXRF for the Investigation of the Deposition Mechanism of Trace Cu Impurities on Si Wafer Surfaces***,* ***K. Baur,*** Stanford Synchrotron Radiation Laboratory*; T. Homma, J. Tsukano,* Waseda University, Japan*; M. Watanabe,* Komatsu Electronic Metals, Japan*; A. Singh, S. Brennan, P. Pianetta,* Stanford Synchrotron Radiation Laboratory

Total Reflection X-ray Fluorescence (TXRF) spectroscopy using synchrotron radiation is one of the most powerful techniques for trace impurity analysis on Si wafer surfaces. In addition, among the more sensitive techniques, it is the only one that is non-destructive. We present the status of the transition metal analysis activity at the Stanford Synchrotron Radiation Labororatory (SSRL) which has matured to a point where a facility exists at which semiconductor companies are able to perform industrially relevant measurements at state of the art detection limits. This facility features clean wafer handling and automated data acquisition making routine analytical measurements possible. The best sensitivity demonstrated to date is 3.4 E7 atoms/cm2 for a 5000 second count time corresponding to 7.6 E7 atoms/cm2 for a standard 1000 second count time. This is more than a factor of 100 better than what can be achieved with conventional TXRF systems. A new development at SSRL is the investigation of the deposition mechanisms of trace metal impurities during a wet cleaning process on Si wafer surfaces. This is considered to be influenced by the oxidation conditions at the silicon wafer surface. This study requires high surface sensitivity and renders Synchrotron Radiation TXRF the technique of choice. We will present our results on the deposition mechanism of Cu trace impurities on Si wafers immersed into ultra pure water, focussing on the correlation between the deposited Cu concentration and the amount of dissolved oxygen present in the ultra pure water.

Magnetic Interfaces and Nanostructures
Room 110 - Session MI+TF-ThA

Magnetic Thin Films and Surfaces I

Moderator: E.E. Fullerton, IBM Almaden Research Center

2:00pm **MI+TF-ThA1 John Thornton Award Lecture - Magnetic Multilayers: Past, Present and Future @footnote 1@***, S.D. Bader*[1], Argonne National Laboratory **INVITED**

Highlights of magnetic multilayer research at Argonne are presented. The most recent past can be taken as the era of giant magnetoresistance multilayers. From there we move to the present where we are addressing issues associated with magnetic pinning across diverse interfaces. Illustrative examples include the coupling between ferromagnets and antiferromagnets, as well as between "hard" and "soft" ferromagnets. The former is of importance in understanding the design of spin valves and magnetic random access memory (MRAM). The later provides a possible nanotech route to the creation of a new generation of ultra-strong permanent magnets. In the future the expectation is that lateral patterning, self-assembly and spintronics will open new vistas. @FootnoteText@ @footnote 1@ This work was supported by the U. S. Department of Energy, Office of Science, under contract number W-31-109-ENG-38.

2:40pm **MI+TF-ThA3 Occupied and Unoccupied Metallic Quantum Well States in the Cu/fccM/Cu(100) [M=Ni, Fe] System***, **A.G. Danese**, R.A. Bartynski,* Rutgers University*; D.A. Arena, M. Hochstrasser, J.G. Tobin,* Lawrence Livermore National Lab & Lawrence Berkeley Lab

Multilayers of alternating magnetic (FM) and non magnetic (NM) layers have attracted a great deal of attention due to their technological importance. We have studied the Metallic Quantum Well (MQW) electronic structure of the prototypical NM/FM/NM systems, Cu/fccM/Cu(100) [M=Ni,Fe], using both angle resolved photoemission (PE) and inverse photoemission (IPE) along the Gamma-bar X-bar direction. We have also used a phase accumulation model (PAM) to calculate the dispersions of MQW electronic states along this axis. The PAM predicts that MQW states will have a high effective mass when they lie in the energy and momentum region of the projected spin polarized band gap of the underlying FM material. PE of the Cu/fccNi/Cu(100) system shows one high effective mass state inside the Ni band gap and another near the gap edge while IPE shows one just above the Ni gap, in good qualitative agreement with the PAM. Numerous MQW states were seen using IPE on Cu/fccFe/Cu(100) but no pronounced high-effective-mass state was seen in the Fe band gap. We believe this can be explained if the Fe film is actually NM which will move the location of the high effective mass states from where they are expected. The PAM also predicts that MQW states will increase in energy as a function of increasing Cu thickness. Although we observed this in our IPE results for MQW states in Cu/fccFe/Cu(100) and PE of Cu/fccNi/Cu(100), our IPE data for Cu/fccNi/Cu(100) show MQW states decreasing in energy with increasing Cu thickness. This same result was observed for Cu films on a Ni(100) single crystal and attributed to lattice mismatch between Cu and Ni, but we have shown that strain cannot account for the behavior of these MQW states and are currently studying how the interface roughness between the Cu and Ni film may provide an explanation. We will discuss our results in the context of the PAM and address the origins of discrepancies between the PAM's predictions and our measurements.

3:00pm **MI+TF-ThA4 The Magnetic Properties of Fe@sub 50@Mn@sub 50@/Cu Multilayers***, **G.J. Mankey**, S. Maat, L. Shen,* University of Alabama*; S.C. Byeon,* University of Alabama, US*; E. Ada,* University of Alabama*; J.L. Robertson, M.L. Crow, T.C. Schulthess, W.H. Butler,* Oak Ridge National Laboratory

The temperature dependent magnetic properties of 50-period multilayers of Fe@sub 50@Mn@sub 50@/ Cu were investigated by squid magnetometry and neutron scattering. Squid magnetometry of a polycrystalline multilayer revealed that field cooling of the multilayer from above the Néel temperature aligns the uncompensated spins, resulting in ferromagnetic ordering of a small fraction of the sample. This ferromagnetic ordering may contribute to the exchange-bias effect observed in Fe@sub 50@Mn@sub 50@/ferromagnet layers. For neutron diffraction measurements, epitaxial multilayers with a fcc (111) surface orientation were produced by magnetron sputtering on H-terminated Si(110). The neutron diffraction measurements reveal a wider mosaic spread in the magnetic lattice relative to the chemical lattice and that only a portion of the Fe@sub 50@Mn@sub 50@ alloy was antiferromagnetically ordered. These observations suggest the domain walls occupy a significant fraction of the Fe@sub 50@Mn@sub 50@ volume. The critical behavior of the antiferromagnetic ordering was determined by measuring the temperature dependence of the magnetic diffraction peak with neutron diffraction. For the first heating cycle, a Néel temperature of 510K and critical exponent of 0.357 are found, consistent with bulk 3D Heisenberg behavior. However, measurements during subsequent heating cycles showed that annealing to 480 K irreversibly changes the microstructure of the multilayer, resulting in a reduction in the magnetization, a reduction of the critical exponent, and an increase of the Néel temperature. XPS depth profiling of the multilayer before and after annealing shows that the interface widths increase due to intermixing of the Fe@sub 50@Mn@sub 50@ and Cu layers. The intermixing is the cause of the changes in magnetic properties. Sponsored by ARO DAAH-04-96-1-0316, NSF MRSEC DMR-9809423, and DOE DMR DE-AC05-96OR22464.

3:20pm **MI+TF-ThA5 Magnetic Reversal of Exchange-coupled Co/Pt Multilayers Probed by Resonant Soft X-ray Scattering***, **O. Hellwig**, S. Maat, E.E. Fullerton,* IBM Almaden Research Center*; J.B. Kortright,* Lawrence Berkeley National Laboratory **INVITED**

The balance between exchange, anisotropy and dipolar energies determines the domain structure in ferromagnetic films. For systems with perpendicular magnetic anisotropy such as Co/Pt multilayers, this often results in stripe domain patterns. In this study we modify the energy balance in Co/Pt multilayers by selectively replacing Pt layers in the structure by CoO or Ru layers. Adding antiferromagnetic CoO layers leads to a perpendicular exchange bias below the Neel temperature of the CoO. The addition of 0.9-nm Ru layers antiferromagnetically couples adjacent Co/Pt blocks and changes the characteristics of the magnetic reversal behavior dramatically. We use resonant soft X-ray small-angle scattering in addition to more conventional methods such as magnetometry and magnetic force microscopy to investigate the domain structure as well as the magnetic reversal process. By measuring both the angle and field dependence of the magnetic scattering we quantify the domain formation during reversal. For the CoO interlayers we find that the domain nucleation process in the biased samples is asymmetric to positive and negative field sweeps but once nucleated the domain patterns are symmetric to the field sweep directions. Zero field cooling in an aligned stripe domain pattern after in-plane demagnetization results in a periodic biasing of the system. At low temperature this leads to a memory effect in the domain pattern that forms during field reversal. The multilayers with Ru interlayers exhibit two distinct reversal modes that reflect the competition between the dipolar and the interlayer exchange energy. Such systems highlight the opportunity to tune the magnetic domain structure and reversal in perpendicular multilayers. Olav Hellwig was partially supported by the Deutsche Forschungsgemeinschaft via a Forschungsstipendium under the contract number HE 3286/2-1.

4:00pm **MI+TF-ThA7 Magnetic Phases of Fe Monolayers on Ni/Cu(001)***, **M. Farle**,* Technische Universitaet Braunschweig, Germany*; H. Poppa,* Lawrence Berkeley National Laboratory

The spin reorientation transition (SRT) of Fe on 4 to 9 ML Ni on Cu(001) is studied by spin-polarized low-energy electron microscopy (SPLEEM) in situ at 295 K. The formation of magnetic domains is monitored during the growth of the Fe monolayers with video rates at a resolution of about 100 nm. The x,y and z components of the magnetization vector are determined. On 8.2 ML Ni/Cu(001) we find three different magnetic phases as a function of Fe thickness. a) 0.2 to 2.8 ML Fe : large out-of-plane magnetic domains, b) 2.8 to 6 ML Fe : large in-plane magnetic domains, c) > 6 ML Fe no magnetic contrast. At the transition from a) to b) which starts at 2.6 ML and ends at 3.0 ML narrow stripe domains appear with a tilted orientation with respect to the film plane. At the transition from b) to c) the size, shape and direction of the in-plane magnetic domains does not change, only the magnetic contrast is lost. This indicates a transition from a ferromagnetic to the paramagnetic state of 6 ML Fe on 8 ML Ni ! Our domain observations are disussed in terms of current concepts of spin-reorientation transitions.

4:20pm **MI+TF-ThA8 Spin-resolved Electronic Structure Studies of Ultrathin Films of Fe on GaAs***, **M. Spangenberg**, E.A. Seddon,* CLRC Daresbury Laboratory, UK*; E.M. McCash,* University of York, UK*; T. Shen,* University of Salford, UK*; S.A. Morton, G.D. Waddill,* University of Missouri-Rolla*; J.G. Tobin,* Lawrence Livermore National Laboratory

Fe thin films of up to 5.5nm were deposited on singular and vicinal GaAs substrates and their magnetic and structural properties investigated by

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[1] **John A. Thornton Award Winner**

spin polarized photoelectron spectroscopy, magnetic linear dichroism in photoemission, magnetization measurements and X-ray diffraction. On both types of substrate the Fe grows predominantly as delta Fe. In agreement with literature results, the magnetization measurements and the magnetic linear dichroism results indicate very similar magnetic properties for the Fe films grown on the two substrate types. However, comparison of the spin polarized valence bands of the Fe films on the singular and the vicinal substrates reveal very significant differences. The possible origins of these observations will be presented. Comparisons and rationalisations will also be made (were possible) between our observations on Fe on GaAs and literature reports for other Fe thin film systems. For example, we have found that the spin polarized valence bands of Fe deposited on the vicinal GaAs exhibit similar features to those reported in the literature for 10nm Fe(100) films on Cu3Au(100) . In contrast, the spin polarized valence bands of Fe films on the singular GaAs are very different to all Fe thin film literature reports, with the differences concentrated in the minority spin channel.

5:00pm **MI+TF-ThA10 Growth Mode Dependence of Magneto Optical Signal Evolution in an Ultrathin Film: Layer by Layer vs. 3D Growth**, ***J.L. Menendez**, G. Armelles, A. Cebollada, J.L. Costa-Kramer,* Instituto de Microelectronica de Madrid (CNM-CSIC), Spain

In this work the magneto-optical properties of the first stadium of the initial growth of a ferromagnetic material deposited on top of a substrate will we analyzed. Two different growth modes will be discussed: layer by layer and three dimensional growth mode. A comparison of the magneto-optical signal for the two growth modes will be presented for three different configurations of the applied magnetic field: magnetic field applied perpendicular to the layer (polar) and in the plane of the layer (transverse and longitudinal). The main results are: In the layer by layer growth mode, the intensity of the magneto-optical Kerr signal is a linear function of the thickness of the deposit layer and the magnetic moment of the layer (i.e., the intensity is a linear function the amount of deposit material for the three configurations). Therefore, the intensity of the magneto optical signal can be used to analyze the evolution of the magnetic moment of the layer as we increase the thickness. In the case of three dimensional growth mode, the intensity of the magneto-optical Kerr signal does not only depend on the magnetic moment of the layer, but also on the shape and amount of islands present in the layer. Contrary to the layer by layer growth mode the intensity of the magneto-optical properties is not a linear function of the amount of the deposited material and therefore can not be directly correlated with the magnetic moment.

Microelectromechanical Systems (MEMS)
Room 130 - Session MM-ThA

Fabrication and Integration Processes for MEMS

Moderator: C.A. Zorman, Case Western Reserve University

2:00pm **MM-ThA1 Integration of a Honeycomb Micromirror with a Surface Micromachined 2D Scanner for Improved Performance**, ***P.R. Patterson**,* University of California at Los Angeles*; G.-D.J. Su, D. Hah,* University of California at Los Angeles, U.S.A*; M.C. Wu,* University of California at Los Angeles

We have developed a novel fabrication process to integrate lightweight single crystal silicon honeycomb micromirrors with surface micromachined 2D scanners for improved optical flatness, compared to polysilicon alone, and improved response, compared to solid (higher mass), micromirrors. The honeycomb micromirrors are formed by silicon fusion bonding of two, silicon on insulator, SOI wafers allowing for precise control of the core and facesheet thickness, here we used 25 µm and 10 µm, respectively. The core SOI wafer is patterned with hexagonal cells of 100 µm long sides and 10 µm thick walls. Design flexibility is an inherent feature of the integrated process, core and facesheet for the honeycomb may be chosen from a wide range of commercial SOI, and the actuator and mirror are developed independently and subsequently bonded with a polymer. The electrostatically actuated 2D scanner with the bonded honeycomb micromirror has a mirror area of 950 µm x 950 µm and an optical scan angle of ±6°. The reduced mass bonded honeycomb micromirror shows an increase in resonant frequency, 158Hz, over an otherwise equivalent solid bonded micromirror measured at 108Hz.

2:20pm **MM-ThA2 Freestanding Microheater in Si with High Aspect Ratio Microstructures**, ***W.-C. Tian**, S.W. Pang,* The University of Michigan

A micromachined gas chromatography system on a chip can be used for environmental monitoring with the advantages of high sensitivity, low power, and portability. To increase sensitivity, a preconcentrator with heating elements and adsorbents is used to adsorb gases and release them at higher concentration to the separation columns. Freestanding, high aspect ratio microstructures in Si are micromachined as preconcentrators. Heat loss to the substrate is minimized by using freestanding heaters to reduce power consumption. A high aspect ratio microheater provides large volume for high adsorbent capacity and hence high sensitivity. Dry etching of Si using etch and passivation cycles has been developed to produce 240 µm thick Si microheaters with 3 µm wide wires, achieving a high aspect ratio of 80:1. This optimized dry etching technology results in high etch rate with vertical profile for thick Si microheaters up to 535 µm. A 400 µm thick Si microheater with 100 µm wide wires, 100 µm gaps, and an area of 9 mm@super 2@ has been fabricated. With the heater on 125 µm thick Si membrane, it takes 850 mW to increase the temperature by 285 °C . The power consumption is reduced to 475 mW for the same temperature raise with freestanding Si microheater. In addition, Si microheaters consist of wires and posts with different conductivity are tested for their heating efficiency. These high aspect ratio, freestanding Si microheaters can provide high power efficiency, large adsorbent capacity, and high mechanical strength as presoncentrators.

2:40pm **MM-ThA3 MEMS and NEMS Physical and Chemical Sensors: Fabrication and Integration**, ***P.G. Datkos**,* Oak Ridge National Laboratory*; T.G. Thundat,* Oak Ridge Natioanl Laboratory*; M.S. Sepaniak,* University of Tennessee **INVITED**

3:40pm **MM-ThA6 Fabrication of Novel Si@sub 3@N@sub 4@ Micromesh Spider Web Bolometer Using Deep Trench Etching on SOI Wafer**, ***M.H. Yun**,* Jet Propulsion Laboratory, Caltech-NASA*; A.M.P. Turner, J.J. Bock, J.A. Podosek,* Jet Propulsion Laboratory

Bolometers are used for sensitive detection of radiation throughout the electromagnetic spectrum, from X-ray to millimeter-wave. The sensitivity of a bolometer can be improved by reducing its base temperature, and reducing its thermal conductivity. Sub-millimeter wave bolometers have achieved a steady increase in sensitivity over the past decade. In this research, we have fabricated and developed extremely sensitive Si@sub 3@N@sub 4@ micromesh spider web bolometers for sub-millimeter astrophysics using microelectromechanical system (MEMS) techniques. The spider-web architecture provides high infrared absorption with minimal heat capacity and volume. We use silicon-on-insulator (SOI) bonded wafers, with a 2 µm of top silicon layer, a 1 µm SiO@sub 2@ insulating layer, and a 350 µm of bottom silicon layer, to fabricate the devices. Using a deep trench reactive ion etching (RIE) from the bottom silicon to the insulating layer, followed by wet etching to remove SiO@sub 2@, a 151-element polygonal spider web array was formed on the 4" SOI wafer. We also observed that the deep trench etching may result in less surface roughness and higher conductivity in the silicon nitride supports. To achieve the best accuracy performance, e-beam lithography is also employed to form contact pad layer. Several Au depositions using photolithography processes form the absorber for optimal infrared absorption, the electrical leads which define the thermal conductance, and the wiring layer for electrical readout. Another silicon wafer is patterned and etched to rest behind the array wafer, forming @lambda@/4 backshorts for maximum optical efficiency. The use of MEMS techniques in this research has improved the sensitivity and format of bolometer arrays. The fabrications of various sub-millimeter device arrays are under development at JPL/Caltech-NASA.

4:00pm **MM-ThA7 Analog Beam Steering Vertical Comb Drive MEMS Actuator**, ***J.J. Fijol**,* Standard MEMS, Inc., US*; J. Prohaska, M. Smith,* Standard MEMS, Inc.*; T. Wester,* ProcessTek, US*; G.W. Tasker,* Standard MEMS, Inc.

The design, modeling, fabrication and characterization of a vertical comb drive actuator are presented. This micro-electro-mechanical device includes a rotating platform supported by two torsion springs and an integrated vertical comb drive actuator. The comb structure was etched into the underside of the rotating platform yielding a compact three-dimensional device. An Au mirror was deposited on the rotating platform and the actuator was used for single axis analog beam steering. The vertical comb design eliminates pull-in, generates large actuation forces (>500 µN) and minimizes the footprint to dimensions approximately equivalent to the size of the mirror (1750 x 2000 µm). Device fabrication required fusion bonding of two wafers; a thick (1000 µm) Si bottom wafer and a top SOI wafer. Deep reactive ion etching (DRIE) was used to etch one half of the comb structure into the substrate wafer and the other half into the handle of the SOI wafer. The mirror platform and torsion hinges were formed in the SOI wafer's device layer using a novel dry release process that eliminated stiction. A matrix of devices were fabricated with varying comb lengths, number of comb fingers and gap spacing (between the upper and lower comb fingers). Devices were operated with a single sided displacement and rotational angles of ~13 degrees were measured for an applied voltage of 200V. Resonant frequency measurements were also performed and the primary resonances were observed between 30 to 200 Hz. Characterization of the mirror surfaces using interferometric microscopy shows the mirror flatness to be better than @lambda@/30 (at @lambda@ = 1550 nm), yielding diffraction limited beam steering.

4:20pm **MM-ThA8 An Integrated MEMS Fabrication Technology Using SU-8 Negative Resists and Conducting Polymers*, S. Li*,** *E. Smela, R. Ghodssi,* University of Maryland at College Park

Tall, narrow channels are necessary for many microfluidics applications, and a simple way to fabricate such channels is desirable. In addition, electrodes are frequently required for fluid pumping. Since polymers can be inexpensive, easy to pattern, and modified to be biocompatible, our goal is to make all-polymer microfluidic systems. EPON SU-8 is a light-sensitive epoxy polymer that can be patterned using conventional UV photolithography. We have previously used it to fabricate high aspect ratio microstructures, and in this work we made channels 15-micron wide and 250-micron deep on top of a patterned gold film on a silicon wafer. Surface micromachining was used (rather than, for example, deep reactive ion etching) to achieve deep channels with straight sidewalls in one simple step. For electrodes, we are investigating the use of conducting polymers such as polypyrrole (PPy). Polypyrrole, which has good biocompatibility, was electrochemically deposited onto the patterned gold electrodes in the bottom of the channel. Thus, the microfluidic channels in the SU-8 had patterned PPy electrodes embedded at the bottom. The two plastic-based MEMS technologies were successfully integrated, demonstrating materials and process compatibility. Preliminary results and a detailed fabrication process for combined SU8 and PPy will be presented.

4:40pm **MM-ThA9 Elimination of Defects on Quartz Plate Surface Induced by Deep Drying Etching and Subsequent Quartz Plate Bonding*, T. Fukasawa*,** *H. Ogawa, Y. Horiike,* The University of Tokyo, Japan

Two issues were studied for fabrication of a microcapillary on a quartz plate in the Bio-MEMS chip. One is generation of the cone-like defects on the quartz bottom surface which were etched deeply with fluorocarbon plasmas. The other is less tight bonding of a pair of quartz plate which is performed at 1.3 MPa, RT and 24 hours following dipping them in a 1% HF solution. In the former issue, we noticed that defects were distributed randomly, nevertheless these diameters were almost same. Increasing RF-s elf bias voltage (Vdc) decreased the number of defects. No defect was observed on the quartz surface at high Vdc of 940V, while the masking Cr film was eroded considerably. The results imply that certain masking materials remain on the quartz surface after its finishing, while AFM and XPS measurement of the surface do not reveal the origin of materials at present. Hence, at first high Vdc of 900V added to the sample during 2 min. to remove the mask materials by sputtering, and then Vdc was decreased down to 500V to etch the quartz plate. Eventually, no defects and high etch selectivity to the Cr mask was achieved. For the latter issue, the quartz bonding mechanism was studied employing an in-situ IR-ATR spectroscopy. 10wt % HF solution was introduced between a quartz plate and a trapezoidal Ge prism whose surface was covered by a sputtered grown SiO@sub 2@ film with 70nm thickness. Elapse time dependence of IR absorption spectra was measured under 5 MPa. H@sub 2@SiF@sub 6@ was observed at the interface and this intensity decreased with increasing the pressing time. Thus the bonding mechanism was considered as follows: At first, H@sub 2@SiF@sub 6@ is produced by etching of SiO@sub 2@ in a HF solution, then it changes to SiO@sub 2@ at presence of H@sub 2@O, thereby acting as a paste layer to bind both surfaces. Based on the mechanism, high strength bonding of quartz plates was performed successfully using a H@sub 2@SiF@sub 6@ solution instead of a 1% HF one.

5:00pm **MM-ThA10 Production Plasma Etching of PZT Structures for Piezoelectric Actuators*, L.G. Jerde*,** *J.P. Almerico, S. Marks, P.F. Werbaneth,* Tegal Corporation

Lead Zirconium Titinate (PZT) is a Perovskite structure dielectric material that is very well suited for piezoelectric actuator applications. The film growth characteristics of PZT and its need for an oxidation barrier effectively limit the choice of electrode materials for the piezoelectric actuator structure to platinum. Neither PZT nor platinum readily form soluble or volatile reaction products. This makes wet etch patterning processes impractical and dry etch patterning processes difficult for PZT based piezoelectric actuator structures. The conventional approach used to pattern these structures utilizes ion milling. The inert ion beam in an ion milling system results in defining the structure by sputter etching material from the exposed surface. The major problem with sputter etching these structures is that the edge of the previously defined PZT layer becomes coated with sputtered Pt atoms during the patterning of the bottom platinum electrode. This results in high leakage currents and limited device performance. We have developed a plasma etch process for photoresist etch masks to eliminate the limitations of ion milling and meet all the production requirements for defining PZT based piezoelectric actuator structures. This process utilizes a patented dual frequency reactor technology, magnetically confined plasma and a combination of feed gases. This technology results in synergistically combining both chemical and sputter etching to successfully meet the requirements for defining PZT based piezoelectric actuators. We shall describe this process and its performance in this paper.

Nanometer Structures
Room 133 - Session NS-ThA
Quantum Dots & Single Electronics

Moderators: J. Murday, Naval Research Laboratory, L. Samuelson, Lund University, Sweden

2:00pm **NS-ThA1 Self-Organized Growth of Semiconductor Nanostructures*, G. Springholz,*** University of Linz, Austria **INVITED**

Strained-layer heteroepitaxy has evolved as a novel method for direct synthesis of self-assembled quantum dots based on the Stranski-Krastanow growth mode where nano-scale 3D islands spontaneously form on the surface of a thin wetting layer. In multilayers, the buried dots tend to influence the dot nucleation in the subsequent layers due to the existence of long range elastic interactions. As a result, vertical and lateral correlations within the dot ensembles are formed, which can lead to a lateral ordering and size homogenization of the dots. Here, it is shown that for various materials systems, different correlated structures are formed depending on the elastic anisotropy of the materials and depending on the growth orientation. As a most prominent example, in IV-VI semiconductor dot superlattices a nearly perfect lateral ordering and a fcc-like ABCABC... vertical stacking of the dots is obtained, and the spacing between the dots can be tuned continuously just by changing of the superlattice period. The basic mechanisms and the limits of the ordering process is discussed on the basis of theoretical calculations and Monte Carlo growth simulations.

2:40pm **NS-ThA3 Applications of Quantum Dots in Photonic and Resonant Tunneling Devices*, L. Samuelson*,** *M. Borgstrom, T. Bryllert, B. Gustafson, S. Jeppesen, M.-E. Pistol, W. Seifert, V. Zwiller,* Lund University, Sweden

3:00pm **NS-ThA4 Single-electron Transistor Based on a 7 nm Gold Particle with Carbon Nanotube Leads*, C. Thelander*,** *M.H. Magnusson, K. Deppert, L. Samuelson,* Lund University, Sweden*; P.R. Poulsen, J. Nygaard, J. Borggreen,* Niels Bohr Institute, Denmark

We have used CVD grown carbon nanotubes to electrically contact an individual 7 nm gold particle by scanning probe manipulation. The result was a single-electron transistor showing a periodic modulation of the current as a function of gate voltage for temperatures up to ~ 200 K. Based on a theoretical fit we conclude that the particle was responsible for the main features of the electron transport, whereas charging effects in the nanotube leads only appeared as a fine-structure. This interpretation could later be verified when the gold particle was removed and the two nanotubes were moved into electrical contact.

3:20pm **NS-ThA5 Control Over Spin Effects in Quantum Dot Structures*, S. Tarucha,*** University of Tokyo, Japan **INVITED**

Experimental studies on a few-electron spin state in semiconductor quantum dots and double quantum dots will be presented. Control and electronic properties of a few-electron spin states and a technical approach for tuning an exchange coupling between two different spin states will be discussed.

4:00pm **NS-ThA7 Probing the Dependence of the Spin Splitting in Quantum Dots on Residual Disorder***, **M. Morgenstern,*** Hamburg University, Germany*; V. Gudmundsson,* Science-Institute, Iceland*; R. Wiesendanger,* Hamburg University, Germany **INVITED**

A scanning tunneling microscope is used to induce a quantum dot into the InAs(110) surface. This quantum dot provides the unique possibility to be moved in a controlled manner across the surface. Thus charged impurities of the substrate are positionable in the quantum dot area (diameter 100 nm). Working at low temperatures (6 K) in magnetic field (6 T) allows to detect the energies of the spin split states corresponding to different Landau indices. While the state energies closely follow the disorder potential in the quantum dot, the energy difference between spin split states does not. From comparison with detailed Hartree-Fock calculations we conclude that this behaviour is directly guided by the non-local character of the exchange-interaction.

4:40pm **NS-ThA9 Electronic Devices Using Single Electron Effects***, **S. Tiwari,*** Cornell University **INVITED**

The single electron effect is a consequence of reduced capacitance in confined islands when dimensions are reduced, usually to the sub-30 nm range. Small capacitances, of the order of aF's, result in a measurable discreteness in the transfer of electrons through the islands because of the large electrostatic energy needed for transfer of charge. In semiconductors, single electron effects occur together with strong quantum-confinement effects due to the smaller density of states. In a single electron transistor, the discrete transfer of the charge is modulated by a gate voltage, and circuits analogous to CMOS can be fabricated. In most single electron memories, the effect of the single electron charge influences transport in a field-effect channel through screening, i.e., discreteness effects are coupled to the traditional field-effect of the transistor. While powerful demonstrations of room temperature operation of single electron transistors, single charge transfer devices, and simple gates with gain have been made, the use of the devices in general purpose electronics is limited by large impedance, low currents, and fluctuation effects. One particularly unique use of single electron transistor has been in charge profiling due to the strong intrinsic charge sensitivity. Memories based on single electron effects, however, are finding wider appeal because of large improvement in power, speed, voltage, and reliability characteristics over traditional non-volatile memory alternatives and their strong compatibility with present-day practice of silicon microelectronics. Such memories have been demonstrated at large dimensions (100's of nm) where numerous discrete nanocrystal islands are employed as well as in the ultimate limits of field-effect when device dimensions reduce to nearly 10 nm in dimension. We will discuss the properties of the single electron device structures and relate them to the underlying physics.

Organic Films and Devices
Room 131 - Session OF+EL+TF-ThA

Electronic Properties of Organic Thin Films

Moderator: M. Himmelhaus, Universität Heidelberg, Germany

2:00pm **OF+EL+TF-ThA1 Interface Formation in Organic Thin Film Transistors: A Photoemission Spectroscopy Study***, **N.J. Watkins**, L. Yan, Y. Gao,* University of Rochester

Pentacene, perylene, and sexithiophene are all materials being used in organic thin film transistors due to their relatively large mobilities. It has been suggested that the functional behavior in organic thin film transistors occurs within the first few molecular layers of the device at the interfaces between the organic and the metals and dielectrics used in fabrication of the thin film transistors. This makes understanding the electronic behavior of the interfaces involved in these devices critical. In order to better understand these interfaces we investigated the interface formation of pentacene, perylene, and sexithiophene on conductors and dielectrics using photoemission spectroscopy to examine layer by layer organic growth onto these materials. We observed indications of dipole formation at the interfaces between the metals and organics for organic on metal deposition, ranging from a 1eV dipole at the interface between sexithiophene and gold to a -0.46eV dipole at the interface between pentacene and calcium. There appears to be a linear relation between the interface dipole and metal workfunction. On the other hand, for metal on organic deposition, more complex material intermixing takes place and as a result, the electronic structure of the interface differs from that of organic on metal deposition. Possible charge transfer, dipole formation and energy level bending at these interfaces will be discussed.

2:20pm **OF+EL+TF-ThA2 Controlling Metallic Contacts to Self-Assembled Monolayers and Molecular Electronic Devices***, **A.V. Walker**, B.C. Haynie, T. Tighe, D.L. Allara, N. Winograd,* Pennsylvania State University

An understanding of the nature of the metal â€“ atom organic monolayer interaction is vital in the development and design of molecular electronic devices. To fully characterize these interactions, we employ a multi technique approach using time-of-flight secondary ion mass spectrometry (ToF SIMS), infrared spectroscopy (IRS), x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Using a methoxy terminated alkanethiol monolayer on Au{111}, we demonstrate that the metal organic monolayer contact can be varied from complete destruction of the monolayer to contact formation at the terminal group to complete penetration through the layer. For metals of intermediate reactivity, e.g. Cu, we observe that the metal atoms interact with the terminal group and penetrate through the layer to the monolayer / Au{111} interface. We have also studied the interaction between promising molecular wire and electronic and device candidates and metal atoms. By using a variety of metals, the formation of the metal molecule contact can also be controlled. This leads us to suggest new metallic contact materials for molecular electronic devices.

2:40pm **OF+EL+TF-ThA3 Dependence of Electrical Properties of Metal/Organic/Metal Systems on Interface Electronic Structure, Morphology and Chemistry***, C. Shen, **A. Kahn,*** Princeton University **INVITED**

Interactions between metals and organic molecules are varied, and depend sensitively on the nature of the metal, of the organic molecule, and on the mode of the formation of the interface. In general, an interface formed by deposition of a metal on an organic film is broader than the interface formed by reverse deposition sequence. Metal atoms diffuse and/or react in the organic layer, acting as electrically active dopant and altering the electronic properties and the structure of the molecular film. These interactions have a profound impact on the injection of charge carriers across these organic interfaces. We present here a comprehensive investigation of these effects performed on a series of metal/organic/metal structures. All experiments are performed in ultra-high vacuum to eliminate extrinsic effects. The organic materials are Alq@sub 3@ (tris-(8-hydroxy quinoline) aluminum), amorphous emissive material extensively used in molecular OLEDs; and F@sub 16@-CuPc (hexadecafluoro copper phthalocyanine), a good electron-transport material that forms molecular stacks. The metals are Al and Au. Combinations of structures including permutations of Al and Au as top and bottom contacts, and even ultra-thin metal layers inserted into the bulk of the organic film, are used to investigate the effects. Key results are: 1. The predominant role of chemistry-induced electronic gap states in leading to identical metal/organic barriers for systems like Al-on-Alq@sub 3@ and Alq@sub 3@-on-Al; 2. the "p-like" doping induced by Au atoms deposited on, and diffused deep into, organic films like Alq@sub 3@ and F@sub 16@-CuPc; and the structural disruption in the F@sub 16@-CuPc stacks resulting from Al-F@sub 16@-CuPc chemical reaction, leading to considerable decrease in electron mobility through the material. General conclusions concerning metal/organic contacts will be discussed. Work supported by the MRSEC program of the National Science Foundation (DMR-9809483) and the NJCOE.

3:20pm **OF+EL+TF-ThA5 Organic Modified Schottky Contacts: Barrier Height Engineering and Chemical Stability***, **D.R.T. Zahn**, T.U. Kampen, S. Park,* TU Chemnitz, Germany*; A. Bushell,* University of Wales Aberystwyth*; M. Rus,* TU Chemnitz, Germany

The electronic properties of metal-GaAs(100)-contacts have been modified using 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA) and dimethyl-3,4,9,10-perylen-tetracarboxylicdianhydride (DiMe-PTCDI). Silver is used as a top electrode. The influence of the organic films on the electronic transport properties was investigated using in situ current-voltage (IV) and capacitance-voltage (CV) measurements. The IV curves show a strong dependence on the modification of the Schottky contacts with PTCDA. The effective barrier height varies between 0.81 ~ 0.64 eV by changing the thicknesses of the PTCDA interlayer between 0 ~ 60 nm. For layer thickness above 60 nm space-charge limited currents in the organic layer determine the carrier transport in the diodes. The CV characteristics do not vary upon introducing an organic interlayer, indicating that the overall capacitance is dominated by the depletion layer within the GaAs substrates and that the width of the depletion region is hardly affected by the PTCDA modification. Therefore, the change in the effective barrier height can be explained by an increasing image-force lowering in the presence of the organic interlayer. The decrease in barrier height as a function of the organic layer thickness is not observed after an exposure of the samples to air. Here, barrier heights are independent of the organic layer thickness and have a value similar to the one of a bare Ag/GaAs(100) Schottky contact. This sensitivity to air is attributed to a reaction of the anhydride groups of the PTCDA with oxygen and/or water leading to carrier type conversion in the organic layer. Similar experiments are currently being performed using DiMe-PTCDI. First results also reveal a comparable decrease in barrier height. In addition, the DiMe-PTCDI modified Schottky contacts are found to be less sensitive to exposure to air because the imide groups are chemically more stable compared to the anhydride groups of the PTCDA.

3:40pm **OF+EL+TF-ThA6 Characterization of Organic/organic' Heterojunctions using UV and X-ray Photoemission Spectroscopies and Luminescence Quenching***, **D. Alloway,*** University of Arizona*; D. Schlettwein,* University of Bremen and University of Oldenburg, Germany*; N.R. Armstrong,* University of Arizona

Heterojunctions based on ultrathin films of perylenedicarboxylicbisimide (PTCDI) dyes, and various phthalocyanine (Pc) overlayers, have been explored using combinations of UPS and XPS, to define the band-edge offset of these systems, and quenching of the luminescence response of the PTCDI layers as a function of coverage of the Pc layer. Depending upon initial PTCDI coverage, the quenching of its luminescence response is extremely efficient using less than 1-2 monolayer coverages of Pc, and can be seen to be due to a combination of energy transfer, and exciton dissociation events. UPS measurements suggest small interface dipoles are formed for some of the PTCDI/Pc heterojunctions, especially those which are based on perfluorinated Pcs, which have high electron affinities. These interface dipoles have the potential to accelerate exciton dissociation, and may be of importance in the application of these systems to organic photovoltaic applications.

4:00pm **OF+EL+TF-ThA7 The Influence of Substrate Interactions on the Metallicity of Polyaniline Films****, **B. Xu,*** University of Nebraska, Lincoln*; J. Choi,* Louisiana State University*; P.A. Dowben,* University of Nebraska-Lincoln

Both Na doped and undoped short chain vapor deposited polyaniline (PANI) thin films were studied using angular-resolved photoemission spectrascopy (ARPES) and X-ray photoemission spectrascopy (XPS). Films, grown on two different substrates, Si and Au, using vapor deposition method show distinctly different properties. Some indication of preferential molecular orientation was observed for ultrathin film deposited on Au substrate, but not on the Si substrates. Clear indication of metallic character was observed for the undoped polyaniline films consistent with recent theory suggesting that for alignment of chain parallel with a metal substrate enhances metallicity. The polyaniline films became more insulating with sodium doping, suggesting that Na doping leads to an increase in insulating behavior that may due to the completion of band filling. @FootnoteText@ *Supported by the Office of Naval Research and the Nebraska Research Initiative.

4:20pm **OF+EL+TF-ThA8 The Electronic Structure Studies of Fluoride Layer Insertion between Al and Organic EL Material@footnote 1@***, **Y. Park,*** Korea Research Institute of Standards and Science, Korea*; J. Lee,* Korea Research Institute of Standards and Science*; D.Y. Kim,* Hallym University, Korea*; S.K. Lee,* Chonnam University, Korea

We have investigated the electronic structures of interfaces between Al and tris-(8-hydroxyquinoline)aluminum (Alq@sub 3@), which is a prototypical organic electroluminescent (EL) material. It has been well known that the insertion of alkali metal fluoride, such as LiF, greatly enhances the EL performance and the origin of such behaviors have been controversial. We used photoelectron spectroscopy techniques including X-ray and UV photoelectron spectroscopy (XPS and UPS) to probe the electronic structures of Al/fluorides/Alq@sub 3@ interfaces. While the presence of LiF layer exhibited enhanced gap states and concomitant formation of shoulder peak in N 1s core level peaks, insertion of other fluorides showed distinctively different behaviors. For example, the presence of MgF@sub 2@ does not form N 1s shoulder peak although weak gap states were observed. Other fluorides including CsF and CaF@sub 2@ are also studied. In addition, the mixture of Al, LiF, and AlF@sub 3@ sequentially deposited on Alq@sub 3@ were investigated. The various core level peaks in this system revealed that this combination does not distinguish LiF and AlF@sub 3@, rather it is more like a homogeneous mixture of LiF, AlF@sub 3@ and Al, which is in contrast to the view that the deposition of Al on LiF/Alq@sub 3@ forms AlF@sub 3@ and liberated Li. We discuss the implications of these results in the electrical properties of the interface and eventually the organic ELD performance that employs this type of electrodes. @FootnoteText@ @footnote 1@ This work was supported in part by MOST of Korea through NRL Program and ASSRC.

4:40pm **OF+EL+TF-ThA9 Direct Observation of Fermi Level Pinning at LUMO in Alkali Metal Doped Organic Films***, **L. Yan,** N.J. Watkins,* University of Rochester*; C.W. Tang,* Eastman Kodak Company*; Y. Gao,* University of Rochester

The electronic structures of pristine and alkali metal doped organic films are investigated using the combination of photoemission spectroscopy (PES) and inverse photoemission spectroscopy (IPES). The lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) can be directly observed by IPES and UPS simultaneously. We found that the Fermi level position in the organic film can be modified by alkali metal doping. For example, in CuPc films, the observed LUMO of the CuPc film is shifted by the Cs doping to less than 0.2eV above the Fermi level. This pinning may be explained by the charge transfer process from Cs to CuPc. Our observation is the direct confirmation of widely used assumption that the LUMO can be inferred from HOMO position in organic films when a valance band shift is observed. The result indicates that energy alignment and charge injection properties of the organic materials can be modified by a simple doping process. Our findings could lead to various interface-engineering methods useful in organic optoelectronic devices. Possible interface dipoles, energy level shifts, charge transfer, metal diffusion and chemical reactions at the interface will be discussed.

Photonics Materials Topical Conference
Room 120 - Session PH-ThA

Photonic Materials: Applications and Processing

Moderator: K.H.A. Bogart, Bell Laboratories, Lucent Technologies

2:00pm **PH-ThA1 Recent Progress on Silica-based Planar Lightwave Circuits for Photonic Networks***, **S. Mino,*** NTT, Japan **INVITED**

The increasing demand for Internet traffic is the motivation for a large-capacity and flexible network. Photonic networks utilizing wavelength division multiplexing (WDM) are expected to meet these requirements. Silica-glass-based planar lightwave circuit (PLC) technologies provide various optical devices for such photonic networks. This paper reviews silica-based PLC devices including arrayed-waveguide gratings (AWG), thermo-optic switches (TOSW), and hybrid-integrated PLC devices with optical semiconductor devices. A PLC is an optical integrated circuit that employs silica glass, which is a stable optical fiber material. Thus the PLC has characteristics that include low-loss, compactness, low-cost, suitability for mass-production, and good reliability. The AWG multiplexer is a key component in dense optical WDM networks, since it is capable of multi/demultiplexing N optical signals of different wavelengths. This is because the multiplexer employs the same system as a grating-based spectrometer. We recently reported a 400-ch AWG multiplexer, which is the largest number of channels yet achieved. An optical switch is required to eliminate the bottleneck in conventional electronic switching systems and the PLC-TOSW is a promising candidate because of its excellent characteristics and reliability. We have already reported 16x16 and 1 x 32 TOSW modules. We can construct a larger-scale photonic switching system with more than 100 ports using these modules. Furthermore we developed hybrid-integration technologies in which optical semiconductor devices can be assembled on a PLC substrate. Using hybrid integration, we can realize a high-speed wavelength channel selector and an optical transceiver for optical access systems.

2:40pm **PH-ThA3 Silica Deep Etching with Vertical and Smooth Sidewall and Reduced RIE Lag***, **D.Y. Choi,** J.H. Lee, D.S. Kim, S.T. Jung,* Samsung Electronics, Korea

Silica waveguides are very important for use in Planar Lightwave Circuits(PLC) because of its low loss and inherent compatibility with silica optical fibers. Deep silica etching(>30um) is necessary when silica PLC is used as a platform to integrate with active devices(LD, PD, SOA, etc.). To lower propagation loss, polarization dependent loss(PDL), and reflectance at waveguide end facet(junction between waveguide and active device), vertical and smooth sidewalls are required. In this work the profile and sidewall roughness of etched waveguides were investigated. Vertical profile was obtained when etching mask was thickened and polymer deposition on sidewall was promoted. But sidewall roughness was increased as deposited polymer thickened. When the clamp in the plasma chamber was changed from alumina to silicon, vertical and smooth sidewall was obtained. RIE lag(Aspect ratio Dependent Etching) becomes important in deep silica etching. We investigated the extent of RIE lag as a function of aspect ratio of trench structures, etching depth, bias power, and pressure. RIE lag increased irrespective of etching depth as aspect ratio increased. When process pressure was high and Si clamp was used, nearly RIE lag-free trench was etched.

3:00pm **PH-ThA4 Development of Integrated Multifunctional Optical Sensors based on III-Nitrides Grown on Si**, ***D. Starikov**, J.-W. Um, C. Boney, A. Bensaoula,* University of Houston

An approach to integrating III-Nitrides-based optoelectronic diode structures into multifunctional optical sensors working in the absorption, scattering, or fluorescence mode is described. The proposed concept is evaluated using an optical sensor prototype assembled from discrete III-Nitrides- and Si-based components coupled to a sapphire window. Testing of this prototype proved the applicability of a wide-range silicon photodetector and UV/blue LEDs in multifunctional optical sensors, and the feasibility of the back-side illumination with a lateral setup of the components. Absorption of light was measured in aquatic polyethylene glycol solutions placed between the sapphire window and a mirror attached in front of it. Observable signals were measured for dilutions ranging from 1000-35000 ppm with a linear dependence for concentrations up to 5000 ppm. The internal reflection from the sapphire window, resulted in a low signal-to-noise ratio, since our prototype did not have any antireflection coating. Scattering measurements were performed using slurries of alumina powder in water at particle concentrations from 6x105 to 4x1012 cm-3. The highest sensitivity and dynamic range is achieved for particle sizes of 0.3-5 mm. The photoresponse dependence is linear for very small (0.05 mm) and very large (15 and 20 mm) particles. Fluorescence measurements of Fluoresceinâ„¢ dye and Chlorophyll in ethanol solutions ranging in concentration from 0.029 to 58 ppm show a more than 6 times wider dynamic range and 5000 times higher sensitivity to the concentration variation than either absorption or scattering measurements. In addition fluorescence shows sensitivity to the pH of the solution. The above results are currently utilized in device modeling, simulation and development of integrated GaN-InGaN multifunctional sensors on Si and sapphire. The talk will present the latest results on the growth, processing, and characterization of these sensors.

4:00pm **PH-ThA7 Application of Photosensitive Methylsilsesquiazane(MSZ) to Lithographic Fabrication of Three Dimensional Periodic Structures**, ***T. Matsuura**, A. Yamada, J. Murota,* Tohoku University, Japan

|> We have proposed a novel lithographic process for fabricating three dimensional periodic structures.@footnote 1@ The essence of the process is that multiple layers of photoresist are coated on the wafer with each layer being exposed with a different pattern without development, and finally after all the photoresist layers are exposed they are developed from upper ones. In this paper, we have applied photosensitive methylsilsesquiazane (MSZ) to enhance the potential of the process. MSZ was spin-coated on the Si wafer, pre-baked at 90°C, and exposed to UV light with a lines-&-spaces mask. Then, the wafer was kept in a moisture case. MSZ contains Si-N bonds, which are converted to alkaline-soluble Si-O bonds after UV-generated photoacid and hydrolysis. Without development of the MSZ at this time, 20nm-thick aluminum is vacuum-evaporated, and then the second photosensitive MSZ was coated. Here, the aluminum layer suppresses mixing of the MSZ layers during coating and penetration of the light to the first layer during exposing the second layer with a different pattern. After these coating and pre-patterning processes are repeated for desired times, the wafers were dipped in a standard developer (TMAH) for MSZ. The areas of the thin aluminum layers wetted by TMAH are also etched, and a periodically stacked structure is formed. When the wafer is cured at 400°C in O@sub 2@, the remaining MSZ is converted directly to methylsilsesquioxane (MSQ) containing stable Si-O-Si networks. As remarkable merits, the present process is simple, easy, and fast, and it possesses intentional-defect-introduction-ability and compatibility with microlithography technology. @FootnoteText@ @footnote 1@ Matsuura et.al, SSDM 2000, p.542.

4:20pm **PH-ThA8 Microphotonics: The Next Platform for the Information Age**, ***L.C. Kimerling**,* Massachusetts Institute of Technology **INVITED**

A rebuilding of the world's information infrastructure is taking place to give instantaneous availability of data, voice and video. This revolution of the Information Age is being gated more by the introduction of new materials and components, than by the design of systems, software and networks. The key frontier is the large scale integration and manufacturing of photonic components to enable the distribution of high bit rate optical streams to the individual information appliance. It is now one-half century since the advent of solid state electronics with the invention of the transistor. Through unparalleled gains in functionality at relatively constant cost, integrated circuits have enabled telecommunications, computation and manufacturing to move to the leading edge of societal change. This revolution has been conducted with "the turn of a single knob": the shrinking of device dimensions. During the last two decades a new "killer technology" has emerged in the telecommunications field. This photonic technology uses optical fibers for interconnection, and has delivered an exponential increase with time of information carrying capacity to the industry. A single optical fiber, with several hundred gigabits/second of capacity, is limited by electronic processing at each circuit node. To avoid this problem direct optical connections are required. To provide full functionality, optical components must be integrated at densities compatible with microelectronic integration. This microphotonics platform represents not only a solution to information access, but it can also solve key problems relating to reliability and complexity that threaten to end the advance of the silicon integrated circuit technology. The Information Age was ushered into existence by Microelectronics. The future will depend on the networking of communications and databases for universal accessibility. This new Age of Connectivity will require a mating of microelectronic and fiber optic technology through integrated of Microphotonic functionality.

Plasma Science
Room 104 - Session PS-ThA
Feature Profile Evolution

Moderator: J.P. Chang, University of California, Los Angeles

2:00pm **PS-ThA1 Predicitve Profile Evolution Simulation in Plasma Etching**, ***V. Vahedi**, D. Cooperberg, L.B. Braly, R.A. Gottscho,* Lam Research Corporation **INVITED**

The ability to predict feature profile evolution as a function of initial patterned profile and process set points will enable reduction in process development time and cost, speed process transfer, and inspire novel process integration approaches. Feature profile simulators have been used in prior studies to qualitatively capture the evolution of both etching and depositing processes. These simulations combined with results from molecular and/or ion beam experiments, chemical analysis of passivation and selvedge layers, plasma diagnostics of density, temperature, and composition have been used to help refine the understanding of the dominant surface mechanisms governing feature evolution and microscopic uniformity. Despite these efforts, our understanding of the complicated surface reaction mechanisms and gas phase kinetics which govern etching and/or deposition of films for commercial applications is incomplete and has prevented truly predictive profile evolution simulations. Commercial etch applications are designed for processing complex film stacks and must meet challenging specifications for mask and stop layer selectivities, sidewall-angle and/or shape, feature width, dense versus isolated feature loading, corner rounding, etch rate, uniformity, and productivity. These demands often require the use of multiple reactive process gases leading to many ion and reactive neutral species. Under these conditions, a semi-empirical approach is the most reasonable way to develop a feature evolution simulation. Our approach is to reduce the complexity of the system using a reduced set of incident species, etch and deposition mechanisms often investigated in the literature under less complex conditions where fluxes have been measured or modeled, blanket etch/deposition rates as a function of reactor settings, and a limited amount of cross-sectional SEM and Langmuir probe data to calibrate the profile simulator. In the current work, we outline a method for calibrating a semi-empirical process simulator and present simulations for Cl2/BCl3 plasma etching of resist patterned Al/0.5%Cu lines. The simulator has been used to predict feature profile evolution as a function of inductively coupled power, RF bias power, and Cl2:BCl3 flow ratio. A silicon trench isolation process simulator may also be discussed.

2:40pm **PS-ThA3 Investigation of Fluorocarbon PECVD from c-C4F8 for use as Passivation during Deep Silicon Etching**, ***C.B. Labelle**, V.M. Donnelly, G.R. Bogart, R.L. Opila, A.M. DeSantolo, A. Kornblit,* Agere Systems

Deep silicon plasma etching is of great importance in fields such as MEMS and photonics. The most commonly used etching technique is the so-called Bosch process, where etch (SF@sub 6@/O@sub 2@) and passivation (c-C@sub 4@F@sub 8@) steps are continuously alternated to achieve vertical profiles. To investigate the passivation step, fluorocarbon films were deposited from c-C@sub 4@F@sub 8@ in a Surface Technology Systems High Rate Advanced Silicon Etch tool, which uses an inductively coupled plasma source. Film deposition rate decreases from 1000 to 740 Å/min as pressure increases from 10 to 25 mTorr, while it increases from 350 to 1500 Å/min as power increases from 300 to 1000 W. Film refractive indices (n) increase roughly linearly from 1.373 to 1.381 for the same pressure range. Carbon 1s XPS shows that, for the ranges explored, pressure and power don't significantly affect the film composition, with films generally consisting of ~ 9% CF@sub 3@, 38% CF@sub 2@, 32% CF, and 21% C-CF. The high CF@sub 2@ and CF fractions correlate with the low refractive indices observed; the slight change in n with pressure is due to replacement of CF@sub 2@ by C-CF as pressure increases. OES data indicate that the C@sub 4@F@sub 8@ is largely broken down into C@sub 2@, F, CF@sub 2@, and CF. Therefore, the films may be formed by C@sub 2@ deposition with subsequent fluorination, CF@sub x@ deposition, or a combination of both. Quadrapole mass spectrometry of the chamber effluents indicates that CF@sub 4@ (50% of effluent), C@sub 2@F@sub 4@ (25%), and C@sub 2@F@sub 6@ (14%) are created. Therefore, recombination, most likely on the walls, can generate larger C@sub x@F@sub y@ species, which also contribute to the film. The effect of residual gases from the etching step on film composition and deposition mechanisms will also be discussed.

3:00pm **PS-ThA4 Ions in Holes - Experimental Measurements of Ion Trajectories Inside Surface Features on rf-biased Wafers***, **J.R. Woodworth,*** Sandia National Laboratories*; I.C. Abraham,* Intel Corporation*; P.A. Miller, R.J. Shul, B.P. Aragon, T.W. Hamilton, C.G. Willison,* Sandia National Laboratories

Most microelectronic devices go though one or more stages in a plasma etching discharge in which energetic ions and radicals are used to etch deep holes or lines in the parts being fabricated. Recent computer models coupled with experimental measurements have greatly improved understanding of the bulk plasmas in these etching discharges. Comparatively little is known for certain however, about interactions between the plasma and the wafer material inside the actual features being etched. This lack of knowledge stems primarily from the absence of experimental data on plasma parameters inside the small surface features. In this talk, we will report direct measurements of ion fluxes, energy distributions, and angular distributions as a function of position at the bottom of small holes in wafers as well as near straight walls and in corners of larger wafer features. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

3:20pm **PS-ThA5 Gate Etching for ULSI Technology : Critical Dimension Control in the sub 0.1 µm Regime***, **X. Detter**, L. Vallier, L. Cunge, O. Joubert,* CNRS/LTM, France*; R. Palla, I. Thomas-Boutherin,* ST Microelectronics, France*; T. Lill,* Applied Materials

In a CMOS process, gate etching is still one of the hottest topic since the accuracy required in gate dimension control is more and more severe. Today, a gate etch process is often composed of a BARC etch step and a polysilicon main etch step, followed by a soft landing step (to preserve the gate oxide) and an overetch step. Each step is individually involved in the critical dimension (CD) control of the gate and contributes to some extent to the CD deviation. In theory, a very precise pattern transfer is possible for each step of the process if : 1) the etching is perfectly anisotropic, 2) the mask dimension is maintained intact during the process (no passivation layer deposition on the mask sidewall and no mask erosion). In practice, for each process step, etch products are deposited on the mask and on the feature sidewalls. The layer formed on the mask sidewalls generates a CD deviation whereas the passivation layer formed on the material being etched protects it against profile deformation. In this talk, a preliminary study of the CD deviation induced by each step of a polysilicon gate etch process is performed and correlated with sidewall analysis by X-ray photoelectron spectroscopy (XPS). Standard chemistries (HBr/Cl@sub2@/O@sub2@) and self clean chemistries (HBr/Cl@sub2@/O@sub2@/CF@sub4@) are compared. In final, for each process step, plasma operating conditions and chemistry are adjusted to minimize the CD deviation of the process and the most promising strategy is proposed.

4:00pm **PS-ThA7 Determination of the Mechanisms Involved in the Creation of the Bowing during the Etching of Deep Anisotropic Trenches in an ICP Reactor***, M. Boufnichel, F. Grangeon,* GREMI, CNRS-Universite d'Orleans, France*; S. Aachboun,* STMicroelectronics, Tours*; P. Lefaucheux,* ***P. Ranson,*** GREMI, CNRS-Universite d'Orleans, France

In this study, we use a cryogenic technique instead of the polymerising one. The cryogenic method has two main advantages: it is faster and cleaner than the classical one, which uses polymerising gas such as C4F8. A cryogenic method with a SF6/O2 chemistry plasma in an Alcatel ICP (Inductively Coupled Plasma) reactor is used to achieve deep trenches with high aspect ratio (>10) and high anisotropy. The etching rate in 2 microns wide and 100 microns deep trenches is about 3.5 microns /min. The slope of the trenches can be adjusted from 88 ° to 90 ° and selectivity to oxide is higher than 300:1. However, profiles need to be improved, mainly by reducing the bowing and undercut effects. Bowing is a local lateral etching located on the side-walls and resulting in profiles destruction while undercut is a lateral silicon etching at the Si/mask interface resulting in trenches larger than the mask opening. One can notice that it is difficult to mask these defects with a cryogenic method without modifying the other features of the etching process such as the etch rate. Bowing creates the most severe damage as the change in profile slope due to bowed surfaces creating voids when it is necessary to refill the trench for a specific application. This study deals with improvements in these effects. We investigated the outcome of process parameters (pressure, bias voltage, temperature, gases flow rates) and mask characteristics (nature, thickness, side slope, trench width) in parallel with electrical and actinometrical measurements using respectively a langmuir probe and optical emission spectroscopy (OES). We also tested several more or less conducting masks (oxide, PSG, Aluminium,...). The different mechanisms responsible for bowing and undercut will be discussed and evaluated.

4:20pm **PS-ThA8 Investigation of Plasma Etching of SiO@sub 2@ Contact Holes using a Statistical Method and a Theoretical Profile Evolution Model@footnote 1@***, **C. Liu**, B. Abraham-Shrauner,* Washington University

The experimental data@footnote 2@ in the plasma etching of SiO@sub 2@ contact holes in a MERIE reactor with a CF@sub 4@/CHF@sub 3@/Ar gas mixture is analyzed by using a statistical method and our semi-analytical etch profile evolution model. The experimental data is from a 2@super 5-1@ fractional factorial experiment design.@footnote 3@ The five factors which are treated as independent variables are the plasma reactor process variables: CHF@sub 3@ flow rate, CF@sub 4@ flow rate, Ar flow rate, gas pressure, and magnetic field. The DC bias voltage, the etch rate, the sidewall slope and the microtrench depth of the etch profiles are analyzed as response variables. The aim of the statistical analysis is the prediction of the measured response variables as a function of the five plasma reactor process variables. The accuracy of the predicted values of the response variables is reported. To reveal the underlying mechanism of the external processing parameter effects on the etch profiles, we simulate the SEMs etch profiles under different processing conditions using our theoretical etch profile evolution model, which is based on the calculation of particle fluxes arriving at the etching surface. Comparison between the control parameters of our model and the measured variables can give us more insights into how to control the etch rate and the etch profile. The new concept of our approach is the combination of the statistical prediction of the measured properties of the etch profile as a function of the reactor process variables and the theoretical simulation of the etch profile. @FootnoteText@ @footnote 1@This research is supported in part by the Boeing-McDonnell foundation. @footnote 2@Melisa J. Buie and Jeremiah Pender supplied the data and SEM micrographs. @footnote 3@M. J. Buie, J. T. P. Pender, and P. L. G. Ventzek, Jpn. J. Appl. Phys. Part 1, 36(7B), 4838(1997).

Semiconductors
Room 111 - Session SC+SS-ThA
Semiconductor Surface Structure

Moderator: R.M. Tromp, IBM T.J. Watson Research Center

2:00pm **SC+SS-ThA1 Direct Surface Structural Determination using Correlated Thermal Diffuse Scattering***, **T. Abukawa,*** Tohoku University, Japan **INVITED**

Since the atomic vibration is strongly correlated among neighbor atoms or within very short-range in crystal, the short-range coherency in electron diffraction may survive even if the long-range coherency is destroyed by thermal vibration. The short-range coherency causes broad structures in the thermal diffuse scattering (TDS). The broad diffraction structures due to short range coherency were indeed observed for a Si(001) surface when medium energy electron diffraction was measured at medium scattering angles.@footnote 1@ The broad features were observed as very simple oscillations of diffracted electron intensity. These features have been termed correlated thermal diffuse scattering (CTDS).@footnote 1@ Since CTDS is well interpreted as kinematical diffraction among nearest neighbor atoms composing the crystal, the three-dimensional Patterson function can be obtained by simple Fourier transformation of a three-dimensional CTDS pattern. When a medium electron beam is incident at a grazing angle, the surface sensitivity of CTDS is enhanced, and the building blocks of surfaces, i.e. the lengths and the orientations of all the surface related nearest-neighbor bonds, can be directly obtained from the Patterson function analysis. The application of Patterson function analysis of CTDS will be demonstrated for the surface structures of Si(001)2x1,@footnote 2@ Si(111)@sr@3x@sr@3-In@footnote 3@ and Si(111)4x1-In. @FootnoteText@ @footnote 1@ T. Abukawa, C.M. Wei, T. Hanano, and S. Kono, Phys. Rev. Lett. 82, 335 (1999). @footnote 2@ T. Abukawa, C.M. Wei, K. Yoshimura and S. Kono, Phys. Rev. B62, 16069 (2000). @footnote 3@ T. Abukawa, K. Yoshimura and S. Kono, Surf. Rev. Lett.7, 547 (2000).

2:40pm **SC+SS-ThA3 Atomic Structures of the of InP (111) Surface***, **C.H. Li**, D.C. Law,* University of California, Los Angeles*; L. Li,* University of Wisconsin, Milwaukee*; R.F. Hicks,* University of California, Los Angeles

The atomic structure of the indium-terminated InP (111), prepared by metalorganic vapor-phase epitaxy (MOVPE), has been characterized by scanning tunneling microscopy (STM), low energy electron diffraction (LEED), and x-ray photoemission spectroscopy (XPS). Three reconstructions are observed depending on the MOVPE process conditions and temperature of annealing in vacuum after growth: these are the (rt3xrt3), (2x2) and (1x1). The (rt3xrt3) reconstruction is the most interesting of these and consists of one ad-atom per unit cell resting on a full layer of indium atoms. This structure is stabilized by the incorporation of oxygen atoms, which are gettered from the MOVPE environment by the indium-rich surface. At the meeting, the atomic structure of each InP (111) reconstruction will be described and compared to those observed on the gallium-rich GaAs (111) and GaN (0001) surfaces.

3:00pm **SC+SS-ThA4 Surface Stress and the Morphology of Si(111) near Tc***, **J.B. Hannon**, J. Tersoff, R.M. Tromp,* IBM Research Division

It is well known that surface stress can strongly influence the structure and chemical composition of surfaces. Despite significant theoretical progress, few quantitative experimental investigations have been reported. One reason for this is the long-range of elastic interactions at surfaces. To quantitatively determine the influence of surface stress, the structure of the surface over micron-scale distances must be precisely known. In this talk I describe low-energy electron microscopy measurements of Si(111) surface structure near the 7x7 to 1x1 transition temperature (Tc = 1135 K), where phase coexistence is observed. We find that the equilibrium domain geometry is determined by a competition between the free energy difference between the phases, which favors a single phase, and elastic relaxation at the phase boundaries, which favors phase coexistence.@footnote 1@ Elastic relaxation occurs because of the difference in surface stress between the two phases. For Si(111), the stress difference has been measured by Twesten and Gibson.@footnote 2@ In equilibrium, the force on each phase boundary vanishes. We use this fact to determine the free energy difference between phases, and phase boundary creation energy, from the measured domain configurations. In equilibrium, each phase boundary gives rise to an independent equation relating the free energy difference, the boundary creation energy, and the stress difference. By measuring domain configurations as a function of temperature, we determine the temperature dependence of the free energy difference between phases near Tc. Our measurements correspond to an entropy difference between the phases of only 0.01 kB per 1x1 unit cell, a surprisingly small value given the fact that the 7x7 structure has long-range order and the 1x1 phase does not. These results indicate that the degree of disorder in the two phases is similar. @FootnoteText@ @footnote 1@J.B. Hannon, et al., PRL, in press @footnote 2@PRB 50, 17628 (1994).

3:20pm **SC+SS-ThA5 Origin of the Wide Si(7 7 17) Domain Parasitic on Si(5 5 12) Surface***, **S.H. Cho**, J. Zhang, J.M. Seo,* Chonbuk National University, Korea

Recently the high-index and single-domain Si(5 5 12) has attracted much attention due to its potential application as a template for one dimensional nanowire fabrication. However, another high-index and single-domain (7 7 17) plane has not been reported yet, although they have similar plane directions of only 0.3 degree off and commonly consist of (2 2 5) and (3 3 7) sections [i.e., (5 5 12)=2x(3 3 7)+(2 2 5) and (7 7 17)= (3 3 7)+(2 2 5)]. From the recent STM investigation on Si(5 5 12), we have detected the wide Si(7 7 17) domains parasitic on Si(5 5 12). Most of wide (7 7 17) domains appear in the terrace adjacent to the step parallel to (-1 1 0) row direction. In a single terrace, the (7 7 17) domain extends to a few hundreds Angstrom from the step, then transforms to (5 5 12). Some (7 7 17) domains are also detected from the bent surface without steps. These wide and pure (7 7 17) domains, appearing near the step or on the bent surfaces, are experiencing the compressed stresses, and these excessive stresses replace the compressed stress originating from a (3 3 7) section in (5 5 12). Therefore, the extra (3 3 7) section is not required in a (5 5 12) plane under such stresses, which results in (7 7 17) domain until such local compressed stresses are released.

3:40pm **SC+SS-ThA6 First-Principles Study of Thermal Fluctuation of Si(111)@sr@3 X @sr@3 - Ag Surface Appeared in Non contact AFM Images***, **M. Tsukada**, N. Sasaki, S. Watanabe,* University of Tokyo, Japan

Until recently ''Honeycomb-Chained-Triangle (HCT)" model for the atomic structure of Si(111) @sr@3 X @sr@3 -Ag surface (referred to @sr@3 -Ag surface hereafter) seemed to be accepted. However, a new structural model called ''InEquivalent-Triangle (IET)" model was proposed by Aizawa et al.@footnote 1@ based on the first-principles calculation as well as the low temperature STM. The IET model is energetically more favorable than the HCT model by about 0.1 eV per @sr@3 X @sr@3 unit cell. In IET model, a mirror plane symmetry is broken and the inequivalent Ag triangles are located in the unit cell. In the present work, we calculated NC-AFM images of IET structure based on a density functional theory. In simulating two-dimensional NC-AFM images, we used a "Fourier expansion method". In this method, the two-dimensional symmetry of the tip-surface system is considered. The thermal averaged images of the fluctuating two different phases of IET structures are calculated in the following way. Namely, at each scanning position of the tip over the surface, the frequency shift is calculated from the force-curve which is obtained from the canonical weighted average of the both phases of IET. The simulated theoretical images reproduces fairly well the experimental observation at room temperature. Therefore our result confirms that the room temperature apparent HCT structure is the thermal fluctuated structures of the two phases of IET. The effect of the tip apex structure on AFM images is also discussed together with the thermal fluctuation. @FootnoteText@ @footnote 1@ H.Aizawa, M.Tsukada, N.Sato and S.Hasegawa, Surf. Sci. 429, L509 (1999).

4:40pm **SC+SS-ThA9 Adsorption of C@sub 2@H@sub 2@ on Si(100) - New High Resolution Core-level Photoemission and Photoelectron Diffraction Results***, M. Kittel,* ***M. Polcik**, J.-T. Hoeft, D.I. Sayago,* Fritz-Haber-Institut der MPG, Germany*; R.L. Toomes, D.P. Woodruff,* University of Warwick, UK

The adsorption of acetylene and ethylene on Si(100) has been subject of a large number of experimental and theoretical studies. Most theoretical studies have favoured a 'di-@sigma@' bonding character for both species, in which the C-C axis lies parallel to the Si dimers with the molecules symmetrically placed atop the dimers. Two independent experimental scanned-energy mode photoelectron diffraction (PhD) studies of the structure of the ethylene adsorption system have provided confirmation of this idea,@footnote 1,2@ but in the case of acetylene adsorption, one such study@footnote 3@ found this atop dimer configuration, but another found a totally different site between two dimers@footnote 2@. In an attempt to resolve this discrepancy we have carried out further experimental studies of the Si(100)/acetylene system at different temperatures and coverages, using high-resolution C 1s photoemission and C 1s PhD. Our new measurements confirm the dominance of the aligned atop-dimer geometry under all conditions studied. We find no direct evidence for a second species, except under conditions associated with fragmentation of the molecular adlayer by the incident soft X-ray beam, although the PhD data could be reconciled with some fractional occupation of other lower-symmetry sites which may contribute only very weak PhD modulations. @FootnoteText@ @footnote 1@ P.Baumgärtel et al, New.J.Phys 1 (1999) 20.1 @footnote 2@ S.H.Xu et al., Phys. Rev. Lett. 84, 939 (2000) @footnote 3@ R. Terborg et al., Phys.Rev.B 61, 16697 (2000).

5:00pm **SC+SS-ThA10 The Effect of an As-flux on the Surface Structure During the Growth of Si on GaAs(001) c(4x4)***, **T.A.R. Müller**[1], B.D. Schultz,* University of Minnesota*; H.H. Farrell,* Idaho National Engineering and Environmental Laboratory*; A. Franciosi,* Universita' di Trieste, Italy and Univ. of Minnesota*; C.J. Palmstrom,* University of Minnesota

Despite the experimental discovery that two atomic monolayers of Si co-deposited with an As-flux are effective in decreasing the barrier height in the Al/Si/GaAs system by 0.5eV, the detailed interfacial atomic structures have yet to be determined. The present work focuses on understanding the evolution of the structure within the first few atomic monolayers caused by the deposition of Si with and without an As-flux on the GaAs(001) c(4x4) surface by MBE. In-situ Reflection High Energy Electron and Low Energy Electron Diffraction, work function measurements, X-ray photoelectron and Auger electron spectroscopies and Scanning Tunneling Microscopy have been used to determine the properties and composition of the surface as a function of Si coverage. For the co-deposition of Si with As, the measured work function increases up to a Si-coverage of 0.5 ML and the intensity ratio of the Ga and As 3d photoemission peaks decreases. However, for Si deposited at pressures <10@super -10@ mbar, the work function shows variations of <50meV from the starting surface and the XPS peak intensity ratio increases for a coverage of 0.5 ML. Atomistic models consistent with electron counting, surface symmetry, work function and composition changes will be presented.

Surface Science
Room 121 - Session SS1-ThA
Catalysis on Model Systems

Moderator: J. Wintterlin, Fritz-Haber-Institut, Germany

2:00pm **SS1-ThA1 Thin Ce@sub x@Zr@sub 2-x@O@sub 2@(111) Films as Model Catalytic Converter Oxygen Storage Materials***, **C.H.F. Peden**, T. He, G.S. Herman,* Pacific Northwest National Laboratory*; Y.-J. Kim,* Taejon National University of Technology*; S. Thevuthasan, V. Shutthanandan, D. McCready, J. Szanyi,* Pacific Northwest National Laboratory

Oxygen storage (OS) materials, usually consisting of ceria (CeO@sub 2@) or modified ceria, are used in automobile catalytic converters to effectively damp deviations in the exhaust air/fuel (A/F) ratio in order to optimize the activity of the precious metal catalyst. We are using thin films of CeO@sub 2@ and ceria-zirconia (Ce@sub x@Zr@sub 2-x@O@sub 2@) as models for fundamental studies of the oxygen uptake, storage, and release properties of these materials. This presentation will emphasize the characterization (by x-ray diffraction, atomic force microscopy, reflection high-energy electron diffraction, low-energy electron diffraction, x-ray photoelectron spectroscopy (XPS) and diffraction, and Rutherford backscattering spectrometry and high-energy ion channeling) of model CeO@sub 2@ and Ce@sub x@Zr@sub 2-x@O@sub 2@ (x = 1.0, 0.9, 0.8, 0.7, and 0.6) thin films will be presented. A wide range of growth parameters using oxygen plasma-assisted molecular beam epitaxy have been used, and successful production of pure-phase, single-crystalline epitaxial oxide films has been achieved for x > 0.6. At higher Zr levels, evidence for phase-separation is observed. We will also report results of XPS and carbon monoxide temperature-programmed desorption experiments that provide evidence for markedly enhanced kinetics of oxygen storage and release upon doping of CeO@sub 2@ by Zr.

2:20pm **SS1-ThA2 Metal and Oxide Particles on Oxide Supports: Vanadium and Vanadia Deposits on Alumina***, **M. Baeumer**, N. Magg, J.B. Giorgi, M. Frank, H.-J. Freund,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

Vanadium in its various oxidation states is a catalytically very interesting system. Oxide-supported vanadia deposits are, for example, used as catalysts for the selective oxidation and dehydrogenation of hydrocarbons. In order to study this multivalent system in more detail, we have carried out model catalytic studies by depositing vanadium under various conditions onto a thin alumina film grown on NiAl(110). Under UHV conditions metallic aggregates are formed. This is connected with extensive changes in the phonon spectrum of the support (intensity damping, frequency shifts and peak broadening). A comparison to other metals, such as Pd, Rh, Ir and Al, reveals that, especially in the low coverage regime, chemical effects at the particle-support interface play an important role. This is also corroborated by XPS. At high coverages, on the other hand, metallic screening seems to gain in importance. If the V deposition is carried out in an oxygen ambient, oxide particles are formed. According to photoelectron spectroscopic data, they have an average oxidation state of +3. Nevertheless, infrared spectroscopy points to the presence of vanadyl groups on the surface of the aggregates actually being a structural element of V@sub 2@O@sub 5@. For both situations, metal and oxide deposits, the CO adsorption and reaction behaviour will be discussed. IR spectra show that CO adsorption on the vanadia aggregates leads to a blue shift of the CO stretching frequency as compared to the gas phase. Interestingly, an interaction between CO and the vanadyl groups is observed. By contrast, CO adsorption on the vanadium aggregates is connected with a red shift. A comparison to the corresponding IR data of other metals (Pd, Rh, Ir)@footnote 1@ underscores the strong metal-support interaction. @FootnoteText@ @footnote 1@M. Frank and M. Baeumer, Phys. Chem. Chem. Phys. 2 (2000) 3723.

2:40pm **SS1-ThA3 Atomic-scale STM Study of Model Catalysts for Hydrodesulfurization***, **J.V. Lauritsen**[2],* University of Aarhus, Denmark*; S. Helveg, B.S Clausen, H. Topsoe,* Haldor Topsoe Research Laboratories, Denmark*; F. Besenbacher,* University of Aarhus, Denmark

Using scanning tunneling microscopy (STM),@footnote 1@ we have recently attained novel atomic-scale information on model catalysts for hydrodesulfurization (HDS), an area that currently receives world-wide attention due to new environmental legislations regarding the sulfur content in fuel. The HDS activity is related to MoS@sub 2@-like nanoclusters promoted with Co atoms located near the edges. Controversy has, however, prevailed since traditional spectroscopy techniques provide no conclusive information regarding the cluster morphology, catalytically relevant edge structures, active sites or promotional effect of Co. We have successfully synthesized ~30Å wide single-layer MoS@sub 2@ clusters on an inert Au(111) substrate as a model system for HDS catalysts. High resolution STM images display an unprecedented view of the atomic details of the MoS@sub 2@ nanoclusters, which contrary to expectations exhibit a triangular morphology. We have also been able to resolve the structures of the catalytically active edges, and from interplay with DFT theoretical calculations we have determined the detailed atomic-scale structure.@footnote 1,3@ The STM images reveal spectacular electronic features near the edge of the triangles, which with input from theory can be associated with electronic edge states. When the MoS@sub 2@-based catalysts are promoted with Co, the STM images directly show a morphological transition from triangular to hexagonally truncated structures. This is driven by a preference for Co to be located at only one type of MoS@sub 2@ edges.@footnote 2@ We are currently investigating the interaction with thiophene, a typical sulfur containing molecule, and preliminary STM results indicate a strong bonding of the molecules to the cluster edges. @FootnoteText@ @footnote 1@ S. Helveg, J.V. Lauritsen et al., Phys. Rev. Lett. 84, 951 (2000) @footnote 2@ J.V. Lauritsen et al. J. Catal. 197, 1 (2001) @footnote 3@ M. Bollinger, J.K. Norskov, private communication.

3:00pm **SS1-ThA4 A Temperature Programmed Desorption Study of Propene Adsorption on Gold Islands Dispersed on TiO@sub 2@(110)***, **H.M. Ajo**,* University of Washington*; V.A. Bondzie,* University of California at Riverside*; C.T. Campbell,* University of Washington

The adsorption of propene on TiO@sub 2@(110) and on gold islands dispersed on TiO@sub 2@(110) [Au/TiO@sub 2@(110)], both at 120 K, has been studied using temperature programmed desorption (TPD), x-ray photoelectron spectroscopy(XPS) and low energy ion scattering spectroscopy (LEIS). Propene adsorbs on both TiO@sub 2@(110) and Au/TiO@sub 2@(110), with desorption peak temperatures of ~190 and ~240 K, respectively, for tiny doses of propene. When only 17% of the TiO@sub 2@(110) surface is covered by gold islands [17% Au/TiO@sub 2@(110)], moderate propene doses populate both the 240 and 190 K TPD peaks, in that order. Since both the dose of propene needed to saturate the 240 K peak and its peak area increase with the gold island coverage, the desorption peak at 240 K is attributed to propene adsorbed at the edges of gold islands. This feature is also seen at about this same temperature even when the gold islands are only one atom thick. Temperature-dependent LEIS results suggest that this propene binds to both a gold island edge and a titanium site. Tiny doses of propene to the 17% Au/TiO@sub 2@(110) surface give the 240 K TPD peak but no 190 K feature. This shows that all of the propene desorbs from these island edge sites. Since some propene molecules must initially physisorb on TiO@sub 2@(110) sites, but no propene molecules desorb from these sites during TPD, the propene must be mobile enough on the TiO@sub 2@(110)

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[1] **Morton S. Traum Award Finalist**

[2] **Morton S. Traum Award Finalist**

surface, either at the dosing temperature or during TPD, to migrate to the gold island edge before desorption (i. e., below 190 K).

3:20pm **SS1-ThA5 Atom-resolved and Nano-scale Structures and Catalyses at TiO@sub 2@ and CeO@sub 2@ Single Crystal Surfaces***, **Y. Iwasawa,*** The University of Tokyo, Japan **INVITED**

This paper presents several important topics in surface catalytic chemistry. Atom-resolved and nano-scale structures of TiO@sub x@ on TiO@sub 2@(110) and (001) surfaces have been visualized by STM and NC-AFM. The surfaces and the TiO@sub x@ structures were transformed to new surface structures in a complicated manner induced by heating and adsorption. Structure models are presented. Carboxylic acids were catalytically decomposed on TiO@sub 2@(110), and the reaction sites and reaction kinetics were characterized by in-situ STM observation. Nano-structures of Pt and Au on TiO@sub 2@(110) were produced by using Pt or Au precursor complexes in different ways. A unique clear-cut size regulation of the Pt particles was found. A new mechanism is presented. Very small Au particles with 0.7 nm height were successfully formed by UV irradiation of the Au-complex adsorbed surface or by UV irradiation of TiO@sub 2@(110) before deposition of the Au complex. Very small Au particles are remarkably active for low temperature CO oxidation. Atom-resolved and cluster structures of and around oxygen defects at CeO@sub 2@(111) surface have also been imaged by NC-AFM. The oxygen defects were mobile even at room temperature. The phenomenon was entirely different from that observed with the TiO@sub 2@ surface, which may be relevant to oxygen reservoir and oxidation activities of CeO@sub 2@ in automobile catalysts and oxidation catalysts. These surfaces are dynamic and reactive, depending on temperature and atmosphere, which may be relevant to the origin and mechanism of catalysis.

4:00pm **SS1-ThA7 Investigations of Size-Dependent Surface Chemistry on Metal Nanoparticles: Dimethyl Methylphosphonate Reaction on Cu/TiO@sub2@(110)***, **D.A. Chen,** J.E. Reddic, J. Zhou,* University of South Carolina

We are interested in understanding how metal nanoparticle size affects surface chemistry so that specific particle sizes with the desired reactivity can be identified for catalysis applications. Cu nanoparticles were grown on a TiO@sub 2@(110)-(1x2) surface and characterized by scanning tunneling microscopy under ultrahigh vacuum conditions. The Cu nanoparticles deposited on TiO@sub2@(110)-(1x2) exhibit the same "self-limiting" growth behavior previously observed on the unreconstructed titania surface: the particle density increases with increasing coverage while particle size is relatively constant. At all coverages, the Cu particles have a uniform size distribution, and the particle size can be controlled by annealing the surface to higher temperatures. Deposition at room temperature produces particles that are ~25 Å in diameter and ~5 Å high, while annealing to 700 K increases the particle size to an average diameter of 60-70 Å and height of 15-20 Å. We found that a smaller size regime of Cu nanoparticles can be prepared by depositing on this highly reduced titania surface compared to the more stoichiometric titania (1x1) surface. X-ray photoelectron studies of the thermal chemistry of dimethyl methylphosphonate (DMMP) on the smallest Cu nanoparticles (25 Å diameter) show that DMMP decomposition occurs below room temperature. Specifically, P-OCH@sub 3@ bond scission is nearly complete at room temperature, but all P-CH@sub 3@ bonds are not broken until much higher temperatures (550 K). Both phosphorous and carbon can be removed from the surface by heating to 800 K. Although studies of DMMP reaction on the TiO@sub 2@(110)-(1x2) surface show that decomposition of DMMP on titania itself commences around room temperature, our data also suggest that P-OCH@sub 3@ bond scission occurs more readily on the Cu nanoparticles.

4:20pm **SS1-ThA8 Catalytic Oxidation of Propylene on Stepped Pt(411): In-situ Mechanistic Studies Over an Extended Pressure Range***, **H.D. Lewis,** D.J. Burnett, A.M. Gabelnick,* University of Michigan*; D.A. Fischer,* National Institute of Standards and Technology*; J.L. Gland,* University of Michigan

Surface defects play an important role in reactivity by, for example, lowering activation barriers for dissociation and increasing the bonding energy of adsorbed species. In this work the catalytic oxidation of preadsorbed propylene has been studied in oxygen pressures up to 0.01 Torr on the stepped Pt(411) surface. Using a combination of kinetic and spectroscopic in-situ fluorescence yield soft x-ray techniques we have characterized the oxidation of propylene. In pressures of oxygen, propylene is completely oxidized by 475 K with oxydehydrogenation preceding skeletal oxidation. The 280 K initiation temperature for oxydehydrogenation is independent of oxygen pressure. The temperature where skeletal oxidation begins decreases from 315 K in 0.0005 Torr oxygen to 300 K in 0.02 Torr oxygen. In the temperature range between oxydehydrogenation and skeletal oxidation a reaction intermediate has been spectroscopically characterized. In-situ catalytic oxidation studies with both propylene and oxygen in the gas phase were also studied. With increasing oxygen pressure the concentration of carbon containing surface species decreases showing competitive adsorption. In this catalytic environment, the onset temperature for deep oxidation decreases with increasing oxygen pressures. Taken together, these results suggest that the inhibition of oxygen adsorption is important in limiting this complex reaction system. This new molecular understanding provides a basis for elucidating the mechanism of this complex surface reaction network.

4:40pm **SS1-ThA9 A Model Catalyst in Action: A Flow-reactor-STM Study of CO-oxidation on Pt(110)***, **B.L.M. Hendriksen,** J.W.M. Frenken,* Leiden University, The Netherlands

The activity of a (model) catalyst can depend on its surface structure. In turn, the surface structure can depend on the reaction conditions. We have used a novel high-pressure, high-temperature scanning tunneling microscope, which is set up as a flow reactor, to determine simultaneously the surface structure and the activity of a Pt(110) model catalyst at semi-realistic conditions for CO oxidation. By controlled switching from a CO flow to an O2 flow and vice versa, we can reversibly oxidize and reduce the platinum surface while imaging the surface with our STM. By simultaneously monitoring the gas composition, we have observed that the formation of the oxide has a dramatic effect on the CO2 production rate. Our results show that there is a strict one-to-one correspondence between the surface structure and the catalytic activity.

5:00pm **SS1-ThA10 The Structures and Phase Transformations of CO and NO on Rh(111) in the Torr Pressure Range Studied by Scanning Tunneling Microscopy***, **K.S. Hwang,** K.B. Rider,* University of California, Berkeley*; M. Salmeron, G.A. Somorjai,* Lawrence Berkeley National Laboratory

Using scanning tunneling microscopy (STM) in a high-pressure reactor cell, we have studied, for the first time, the molecular structure and reaction of CO and NO on Rh(111) in the Torr pressure range. This is a model system for the automobile catalytic converter, where CO is oxidized to CO@sub 2@ and NO is reduced to N@sub 2@. Numerous reaction studies have been done in various temperature and pressure regimes,@footnote 1@ but they generally do not yield direct information about molecular surface structure. Traditionally, molecular surface structure studies have been done at low temperature and pressure. These structures are kinetically frozen however, and may be different from high-temperature, high-pressure structures that are in equilibrium with the gas phase. At high coverage, CO forms a (2x2)-3CO structure on Rh(111) with one top-site and two hollow-site molecules in the unit cell.@footnote 2@ This structure forms at 300 K from low pressure to at least atmospheric pressure. NO at 300 K forms an analogous structure below 0.03 Torr. Above 0.03 Torr we have discovered a new structure with a (3x3) unit cell. By directly observing the phase transformation between the two structures, we have found the heat of adsorption of the new structure to be 0.9 eV and an energy barrier between the two structures of 0.7 eV. When CO and NO are coadsorbed on Rh(111) at low partial pressures of NO, NO appears to mix randomly among the CO molecules. As the partial pressure of NO increases, the NO segregates into islands. The (3x3)-NO structure nucleates on these islands, though the presence of CO on the surface inhibits the phase transition until the NO partial pressure is three to five times that of CO. At temperatures above 300 K, we have seen evidence of the reaction between CO and NO occurring. @FootnoteText@ @footnote 1@ V. P. Zhdanov and B. Kasemo, Surf. Sci. Rep. 29 (1997) 31. @footnote 2@ M. A. Van Hove, R. J. Koestner, and G. A. Somorjai, Phys. Rev. Lett. 50 (1983) 903.

Surface Science
Room 122 - Session SS2-ThA
Nucleation & Growth

Moderator: P.A. Thiel, Iowa State University

2:00pm **SS2-ThA1 The Use of Instabilities in Epitaxial Growth for Lateral Patterning of Surfaces***, **H.-J. Ernst,*** CEA Saclay, France **INVITED**

The use of intrinsic instabilities in growth processes is currently actively explored as a promising pathway to reach a lateral patterning of surfaces at the nanometerscale. The origin of these instabilities is traced back to the presence of an excess energy barrier for adatom diffusion over descending steps, the Ehrlich-Schwoebel barrier. Structural patterns can be created either by spontaneous self-organization of the material deposited, or by guided growth on prestructured substrates. The deposition of Cu on singular and vicinal Cu surfaces illustrates this approach, using Helium Atom Scattering (HAS), Scanning Tunneling Microscopy (STM) and Low Energy Electron Microscopy (LEEM) as structural probes. Surprisingly, the interaction of green laser light with these surfaces leads as well to atomic scale restructuring. @FootnoteText@ I like to acknowledge the contributions of F. Charra, L. Douillard, R. Gerlach, and T. Maroutian at various stages of this project.

2:40pm **SS2-ThA3 Evolution of Mounds during Ag/Ag(100) Homoepitaxy: Temperature Dependence of Pre-asymptotic Behavior***, **K.J. Caspersen**, A.R. Layson,* Iowa State University*; C.R. Stoldt,* University of California at Berkley*; V. Fournee, P.A. Thiel, J.W. Evans,* Iowa State University

Step edge barriers are known to induce unstable epitaxial growth characterized by "mound" formation, but a detailed understanding of the roughening and coarsening dynamics is lacking. Most theoretical studies aim to elucidate asymptotic behavior for simple models in the regime of (mound) slope selection. We instead perform realistic atomistic modeling of Ag/Ag(100) growth where slope selection is often slow, and the experimentally relevant "pre-asymptotic" behavior is then characterized by slow coarsening and rapid roughening. To describe observed 25ML morphologies from 150-300K ,@footnote 1@ our model includes irreversible island formation (with a 0.40eV barrier for terrace diffusion), distinct step edge barriers for straight and kinked step edges (0.07eV and ~0eV), and a realistic description of periphery diffusion which controls island shapes and coalescence (rapid diffusion along straight steps; 0.41eV barrier for kink rounding). This model then reproduces the key features of mound evolution observed at various temperatures for growth up to 60-100ML, it allows a precise characterization of evolution of the mound distribution (as quantified by a suitable tessellation), and also reveals the crossover to slope selection for thicker films. @FootnoteText@ @footnote 1@K.J. Caspersen et al., Phys. Rev. B 63 (2001) 085401.

3:00pm **SS2-ThA4 Mechanisms for Hole Formation in Surface Alloy Systems: Rh/Ag(001)@footnote 1@***, **L.D. Roelofs**,* Haverford College*; R.J. Behm,* University of Ulm, Germany*; D.A. Chipkin,* Haverford College

We present a study of mechanisms for surface hole formation during heterogeneous, metal-on-metal epitaxial growth of surface alloy systems. We consider specifically the system Rh/Ag(001) for which a detailed STM study of the structures formed during epitaxy at room temperature is available.@footnote 2@ Three mechanisms are proposed and investigated via a kinetic Monte Carlo simulation based on a simple model for the atomic-level energetics. It is found that the dominant mechanism of hole formation in this system involves the growth of vacancy islands via an upward exchange diffusion move. First principles total energy computations using the VASP suite of programs confirm the plausibility of the explanation. Our simulation also accounts, via the same mechanism, for the observation of the growth of Ag islands on top of deposited material. An alternative mechanism for hole formation, coalescence of point vacancies, is found not to contribute appreciably to formation of vacancy clusters, but point vacancies do catalyze structure formation by other means. The mechanism identified in the present study should be applicable to other soft substrate surface alloy systems. L.D.R. thanks the DOE for supporting a visit to Sandia Livermore in order to carry out the VASP calculations.. @FootnoteText@ @footnote 1@Funded by the NSF via grant DMR - 9974545 @footnote 2@S.-L. Chang, et al., Phys. Rev. B53, 13747 (1996).

3:40pm **SS2-ThA6 Molecular Dynamics Simulations of Thin Film Nucleation through Molecular Cluster Beam Deposition: Effect of Incident Angle***, **Y. Hu**[1],* The University of Kentucky*; S.B. Sinnott,* The University of Florida

Deposition of organic cluster beams on surfaces leads to the creation of polymeric thin films through rapid chemical reactions. These reactions occur over timescales on the order of a few picoseconds and therefore are suitable for study by molecular dynamics. Besides such factors as incident energy and cluster size, the deposition angle is believed to have important effects on the nucleation of thin films grown through molecular, ionic and cluster beam deposition. In this work, angular effects on molecular organic beam deposition are studied extensively through classical molecular dynamics simulations. The reactive empirical bond potential developed by Brenner et al.@footnote 1@ is used in this simulation. Various organic cluster beams are deposited on the hydrogen terminated diamond (111) surface at room temperature. The beam impacts the surface along different crystallographic orientations at incident angles of 0Â°, 15Â°, 45Â° and 60Â° with respect to the normal to the surface. Two beam energies are considered: one corresponding to 25eV/cluster molecule and one corresponding to 50eV/cluster molecule. As the angle increases from the normal, the amount of energy deposited along the surface normal decreases. Therefore we have also considered cases where the energy normal to the surface is constant while the total energy varies. The results show the dependence of the angle effects on the crystallographic orientations, the incident energies and the reactivity of the impacting species. This work is supported by the National Science Foundation (CHE-9708047). @FootnoteText@ @footnote 1@S.B.Sinnott, L.Qi, O.A.Shenderova, D.W.Brenner, in Chaper 1 Volume 4 of Advances in Classical Trajectory Methods, Molecular Dynamics of Clusters, Surfaces, Liquids, and Interfaces, Ed. W. Hase(JAI Press, Inc. Stamford, CT, 1999), p. 1-26.

4:00pm **SS2-ThA7 Scanning-tunneling/Atomic-force Microscopy Study of the Growth of KBr Films on InSb(001)***, **J.J. Kolodziej**, B. Such, P. Czuba, P. Piatkowski, F. Krok, M. Szymonski,* Jagiellonian University, Poland

Thin epitaxial KBr films have been grown on InSb (001) surface. Scanning tunneling and non-contact atomic-force microscopy in ultra-high vacuum has been used to study surface structures generated during growth, for coverages ranging from 0.3 to 120 ML. It is found that in submonolayer coverage regime oval-shaped islands of monatomic thickness are formed. These islands are often cut along crystallographic direction and the distribution of these islands on the substrate surface is anisotropic reflecting anisotropic diffusion of KBr molecules during the growth. The KBr/InSb interface is likely to be stabilized by a bond between the halide ion and AIII atoms arranged in chains on InSb. At 1 - 1.5 ML coverage continuous KBr film is formed and the material in excess of 1 ML forms rectangular islands with edges oriented along and directions on the surface. For multilayer coverages pyramidal structures of rectangular bases are formed indicative of slow diffusion of KBr molecules down across steps. These rough KBr films can be, as a result of thermal annealing, converted to flat films exposing large (> 0.1 micrometer), atomically flat (100) terraces.

4:20pm **SS2-ThA8 In situ Variable Temperature-pressure STM on Selected Nanoparticles: From Nucleation and Growth to High Pressure Stability***, **A.A. Kolmakov**, D.W. Goodman,* Texas A&M University

The nucleation and stability of metal nanoparticles on oxides are of great importance in catalysis, gas sensors and microelectronics. Using variable temperature and pressure scanning tunneling microscopy (STM) in conjunction with in-situ deposition techniques, a versatile imaging approach has been developed that allows the nucleation, growth and alloying of individual nanoparticles to be followed in-situ. Selected nanoparticles can be exposed to reactive gas mixtures and the evolution of their morphology followed while spanning a pressure range of over eleven orders of magnitude. Since the size and composition of the particles can be controlled individually, direct comparison of various particles with similar treatments can be carried out in a single experiment. In particular, the stabilities of Au and Ag nanoparticles supported on TiO@sub 2@ (110) have been investigated while carrying out a catalytic reaction (CO oxidization) and while exposing the sample to an aqueous environment.

4:40pm **SS2-ThA9 Characterization by XPS, LEED and STM of Silicon Deposited onto HfB@sub 2@ (0001)***, **R. Singh**[2],* University of Illinois at Chicago*; W. Hayami, T. Tanaka,* National Institute for Materials Science, Japan*; M.W, Trenary,* University of Illinois at Chicago

In the microelectronics industry, transition metal diborides like TiB@sub 2@ and HfB@sub 2@ have received a great deal of attention as possible diffusion barriers because both diborides are refractory materials that have high melting points, high degrees of hardness, and are chemically very stable. While studies have been done to assess the ability of these materials to prevent the diffusion of copper into silicon, there have not been any studies of the actual bonding, or interface, between silicon and a diboride. Since the structures and composition of the interfacial region necessarily dictate the properties and morphology of the subsequent film, this region is of great importance. Also, while HfB@sub 2@ on Si more closely resembles the actual application of a diffusion barrier, many experimental advantages are gained from studying Si on HfB@sub 2@, while yielding the same results as HfB@sub 2@ on Si. Silicon was deposited onto a clean and well ordered single crystal by the reaction of silane, SiH@sub 4@(g), at 800C. Two phases of hafnium and silicon, were

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[1] **Morton S. Traum Award Finalist**

[2] **Morton S. Traum Award Finalist**

identified on the surface. The Hf@sub 5@Si@sub 3@ phase has a hexagonal unit cell and was found to form hexagonal islands that were more than 100Å in width and scattered over the surface. This surface exhibited a complex (@sr@7x@sr@7)R19.1 LEED pattern and two distinct XPS peaks in the Si2p region at 99.8 and 99.4 eV assigned to silicon and the silicide respectively. The HfSi@sub 2@ phase has an orthorhombic unit cell and formed nanometer-wide lines which, at higher coverages, form a "wagon wheel" structure. STM also shows rows of silicon dimers both before and after the 900C anneal, growing side by side the silicide features. These dimers are "bean-like" protrusions that have a (@sr@7x@sr@3) silicon structure. After annealing the dimer covered surface to 1300C the Si-Si bond was cleaved and the individual silicon atoms relaxed to form a honeycomb-type structure, occupying the three fold hollow sites.

5:00pm **SS2-ThA10 Heteroepitaxy of a Manganese Carbonate on Calcite in Aqueous Solutions***, **A.S. Lea**, A. El-Azab, D.R. Baer, J.E. Amonette,* Pacific Northwest National Laboratory

Heteroepitaxy of a manganese carbonate phase on the (1014) surface of calcite using an AFM has been observed in solution when the ion activity product of Mn@super 2+@ and CO@sub 3@@super 2-@ exceeds the solubility limit of MnCO@sub 3@. Thermodynamic data indicates that the resulting phase is a Mn@sub 0.5@Ca@sub 0.5@CO@sub 3@ phase and is consistent with our XPS and EPR measurements. These islands, while growing many microns in length along the [221] direction, have a uniform width of 150-220 nm and a uniform height of only 2.5 nm, corresponding to eight atomic layers. The islands cease growing when they encounter a step edge and have been observed to dissolve when undercut by a growing etch pit. Comparison of the crystal lattices of calcite and the Mn@sub 0.5@Ca@sub 0.5@CO@sub 3@ phase, indicate the direction of preferred growth is along the direction of greatest lattice mismatch, 3.3% as opposed to a mismatch of 2.2% along the direction of island width, [010]. A 25% decrease in stiffness along the [221] direction compared to the stiffness along the [010] direction is sufficient to account for this discrepancy. We have used a glued wetting layer model with conditions of constant surface chemical potential to model the observed morphology of the heteroepitaxial layer. Although not all the required parameters are accurately known, the model accurately depicts the measured cross-sectional profiles of the islands. This result implies that the models and considerations associated with nano-phase formation on surfaces in vacuum apply to a significant degree to growth in solution. @FootnoteText@ Pacific Northwest National Laboratory is a multiprogram national laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RL0 1830.

Thin Films
Room 123 - Session TF-ThA
Emerging Thin Film Techniques

Moderator: T.M. Klein, University of Alabama

2:00pm **TF-ThA1 Ionized-PVD with Quasi-Stationary High Power Magnetron Sputtering***, **U. Helmersson**, J. Alami,* Linköping University, Sweden*; A.P. Ehiasarian,* Sheffield Hallam University, UK, United Kingdom*; K.M. Macák,* Sheffield Hallam University, UK*; J.T. Gudmundsson,* University of Iceland, Iceland **INVITED**

The development of ionized-PVD by sputtering over the last few years is based on the production of a high-density plasma (10@super 18@ - 10@super 19@ m@super -3@) in front of the source. As the atoms pass through this dense plasma, a large fraction becomes ionized. The high plasma densities can be achieved in several ways, by using an rf-coil, a hollow cathode arrangement, or as in the present case, simply by increasing the power supplied to the magnetron source. To avoid extensive heating of the cathode as well as the development of arcs, in the latter case, the power is pulsed with a duty factor of around 1 %, which maintains the average power at an acceptable level. In the present work, peak power densities of several kW cm@super -2@ with a repetition frequency of 50 Hz was used. This technique has been demonstrated for sputtering a range of different metals, yielding a degree of ionization of 30 to 70 % depending on cathode material and applied power as measured for Cu, Ta, and Cr cathodes. Optical emission studies demonstrate a temporal development of the plasma during the pulse. Initially the emission is dominated by Ar-lines, but later in the pulse lines from cathode-metal ions dominate the emission. This may indicate a transition from Ar-sputtering to self-sputtering during the pulse. That self-sputtering occurs is also supported by the observation that the relative deposition rate (pulsed rate as compared with normal dc rate) scales with self-sputtering yield giving low relative deposition rate for low-yield materials. Film growth by this sputtering technique is demonstrated in trench-filling applications, reactive sputtering of chromium nitrides, and for carbon films.

2:40pm **TF-ThA3 Ionization of Sputtered Titanium Atoms in Radio Frequency Magnetron Sputtering***, **K. Okimura**, T. Nakamura,* Tokai University, Japan

Recently, the ionization of the sputtered flux has received much attention for several aspects such as, assisting effect of low temperature crystallization, filling characteristics to high aspect ratio seed layer and damage in integrated circuits. We have investigated sputtered titanium(Ti) atom densities for both Ar discharge and Ar-O@sub 2@ reactive discharge by means of atomic absorption method.@footnote 1@ As for the ionization of sputtered atom, quantitative measurement is lacking for understanding ion flux incident to substrate. In this study, optical emission spectroscopy for Ti ions were performed using 250 mm monochromater in planar rf magnetron sputtering apparatus with 100 mm diameter titanium target and 35 mm electrodes spacing. Atomic absorption method using a hollow cathode lamp was also applied in order to evaluate concentration of Ti ions. A series of optical emission originated from Ti ion, 336.1 nm, 337.3 nm and 338.4 nm, were observed in a spectrum at argon pressure of 3.5 Pa and radio frequency power of 200 W. We discussed the ionization of sputtered atoms from relative intensities of ionic optical emission to atomic emission in measured spectra. Radial(r) and axial(z) profiles of optical emission intensity of Ti ions at 336.1 nm for different discharge conditions such as rf power, Ar pressure, were presented. At axial directions, z=15 mm, 21 mm, 27 mm, maximum emission of Ti ion located at radial position around r=35 mm where was slightly outward position compared to the position with maximum strength of transverse magnetic field. Absorption measurement of 336.1 nm line showed absorption intensity around 10@super -2@ indicating ionization degree less than several percent for sputtered Ti atom density. Plasma parameters and mass-resolved analyses of incident ions were served for discussion on mechanism of ionization and ion flux incident to substrate. @FootnoteText@ @super 1@T.Nakamura and K.Okimura : to be appeared in JVST-A.

3:00pm **TF-ThA4 High Rate Growth of Cu Thin Films Using New Magnetron Sputtering Source***, H.K. Park,* Sungkyunkwan University, Korea, South Korea*; K.H. Nam, J.G. Han, **J.-H. Boo**,* Sungkyunkwan University, Korea

We have deposited the copper (Cu) thin films on Si(100) and stainless steel substrates in the growth temperature between room temperature and 500 °C using pulsed D. C. magnetron sputtering method. An unbalanced magnetron sputtering source with high current (20 - 120 mA/cm @super 2@) and low voltage (100 - 1000 eV) was designed and constructed for high rate deposition. Based upon the results of magnetic field simulation, we built-up the highest power (120 W/cm @super 2@) Cu magnetron sputtering source to enhance the sputtering yield and film growth rate. The maximum deposition rate and sputtering yield of the newly developed sputtering source are 2.8 µm/min. and 70%, respectively. When an ion extraction grid was adapted between the Cu target and substrate, however, the growth rate was increased over 3 µm/min. This is 10 times higher than that of conventional sputtering method, and the sputtering yield was also reached to 80% due to low voltage and high current Cu-accelerated ions. XRD and XPS showed that highly oriented polycrystalline Cu(111) thin films with no impurity were obtained on the stainless steel substrates. During film deposition, plasma diagnostics was also carried out in situ by optical emission spectroscopy analysis. Electrical conductivity was also measured with four-point probe method.

3:40pm **TF-ThA6 Low Temperature Hollow Cathode Sputter Deposition of Al@sub 2@O@sub 3@ Thin Films***, **A. Pradhan**, S.I. Shah, K.M. Unruh,* University of Delaware

Hollow cathode sputtering offers a novel way of conformally coating three-dimensional objects. It offers the added advantages of uniform sputtered flux and high plasma density. We have characterized a Hollow Cathode Source (HCS) for depositing alumina thin films by reactive sputtering. The target potential decreased sharply in the poison mode. This is contrary to what is observed in most reactive sputtering systems. This was attributed to the large secondary electron emission coefficient for Al@sub 2@O@sub 3@. The hysteresis behavior of planar sputtering was not observed. High growth rates at low power densities were obtained even in the poison mode. This was probably due to the enclosed geometry of the hollow cathode and very high cathode to anode area ratio. The oxidation state of the film was determined using X-ray Photoelectron Spectroscopy (XPS). The alumina content of the films increased sharply with the addition of oxygen to the system. Above a certain oxygen concentration pure Al@sub 2@O@sub 3@ films were obtained. A low cost high deposition rate method for depositing crystalline alumina films will be presented.

4:00pm **TF-ThA7 Influence of the Growth Conditions of AlN Films by Laser Ablation***, **A. Basillais**, C. Boulmer-Leborgne,* GREMI, France*; J. Perriere,* GPS, France

The pulsed laser ablation of targets in vacuum or in a reactive ambient gas (especially for oxide layer) is a very popular method for growing thin films with complex compositions and various properties. But the reliability of the pulsed laser deposition technique needs a wider understanding of thin film growth for nitride films. In this study we report AlN thin film growth by pulsed laser ablation of Al target in N2 reactive ambient gas compared to laser ablation of AlN target in vacuum or N2 gas. An approach of AlN film grown on Si(100) and Al2O3 substrates is studied. The best experimental conditions are defined in relation with film quality deduced from surface analysis (RBS, NRA, XPS, XRD, MEB). The influence of process parameters such as nature of the target, laser energy density and nitrogen partial pressure on the composition, chemical nature and structure of the films has been investigated. The main problem in AlN film growth was the oxygen incorporation. The origin of this contamination and the mechanisms of incorporation were studied, and the crucial parameter was found to be the residual pressure during ablation. Due to the difference in chemical reactivity between O and N, it is necessary to increase the density of atomic nitrogen to obtain pure AlN films. Thus, a RF discharge device was added allowing a better nitrogen molecule dissociation. Finally the hexagonal AlN phase can be formed in the laser deposited films. Highly textured films presenting epitaxial relationships with (001) Al2O3 substrates can be grown with only 5% oxygen contamination. The plasma plume investigation by emission spectroscopy allows the reactive species kinetics study for AlN growth. A secondary discharge device is mounted on the substrate to study the dark zone where there is no more plasma plume emission.

4:20pm **TF-ThA8 Low Temperature and Plasma Damage Free Deposition of Silicon Dioxide on Novel Film Deposition Method Called a Radical Shower-CVD (RS-CVD)***, **A. Kumagai**, K. Ishibashi, X. Ge, M. Tanaka, H. Nogami, O. Okada,* Anelva Corporation, Japan

A novel film deposition method called a Radical Shower-CVD (RS-CVD) has been developed for high quality gate-oxide film formation on low temperature Poly-Si TFT-LCD fabrication. RS-CVD has the advantages of both conventional plasma enhanced-CVD and remote plasma-CVD without having their disadvantages and is characterized by plasma damage free deposition on a large area substrate at a low temperature of about 300°C. As a silicon dioxide film is deposited on the substrate through the diffusion of SiO@sub2@ formed by the reaction of oxygen radical with SiH@sub4@ in the gas phase, oxygen radical quantity, distance from gas injection to substrate, and deposition pressure are very important as a control factor of gas phase reaction. Dependencies of film quality on those factors are investigated to confirm the optimization methods in RS-CVD film deposition process. The calculation of the gas phase elementally reaction have been performed to discussion the formation mechanisms of SiO@sub2@. As a result of this study, it was confirmed to be important in suppressing the contamination of the elements including the OH bonding groups in the films during the deposition itself. The oxygen radical quantity, the distance from gas injection to substrate, and the deposition pressure were useful to control the speed of overall reaction and the elements arriving at the substrate. It was important in the film properties to control the residence time of gases until they reach the substrate by adjusting those factors mutually.

Vacuum Science & Technology
Room 125 - Session VST-ThA

Total & Partial Pressure Gauges & Their Calibration

Moderator: R.W. Dobrozemsky, Vienna University of Technology, Austria

2:00pm **VST-ThA1 Partial Pressure Measurements at milliTorr Pressure using a Miniature RGA with an Electron Multiplier***, **R.E. Ellefson**, L.C. Frees, T.L. Karandy,* Inficon, Inc.

Operation of an extended pressure range (XPR) miniature residual gas analyzer at millitorr pressures allows direct measurement of process gases involved in physical vapor deposition without the need for pressure reduction and associated pumps. A new electron multiplier (EM) capable of sustained operation at all XPR operating pressures (up to 20 mTorr) extends the measurement speed at process pressure while maintaining nanoTorr detection limits at base pressure. Design features that allow the EM to operate continuously at high pressures are presented together with data that shows that a gain of 100 is optimum for practical measurements of gas species from 10@super -9@ to 10@super -2@ Torr. A comparison of the operation of the XPR with a standard RGA shows each instrument has a similar dynamic range of ion currents but the pressures producing the currents are shifted two decades of pressure higher for the XPR. The physical phenomena of ion-molecule reactions do occur at millitorr pressures but do not interfere with useful measurements of the impurities in Ar sputtering gases or the detection of contaminants (like photoresist) in degas chambers. Examples are given of ion molecule reactions, e.g. N@sub 3@@super +@ and Ar@sub 2@@super +@ produced at pressures of 10 mTorr for N@sub 2@ and Ar, respectively.

2:20pm **VST-ThA2 The Use of a Quadrupole Residual Gas Analyser to Automatically Verify the Purity of Tokamak Fuelling Gases***, **R.J.H. Pearce**, A. Henshaw, J. Bruce, S. Bryan,* EURATOM/UKAEA Fusion Association, UK

It is essential that the gases injected into the JET experimental fusion tokamak be as requested and free from contamination. To give maximum flexibility a matrix architecture is used to handle the many different gases which can be introduced. In addition to problems of human error and contaminated gas bottles, the matrix architecture provides the potential for gases to become cross-contaminated either through valve leakage or due to control problems. A gas species verification system has been designed and commissioned to automatically confirm on-line the conformity of the gas being supplied to the torus. The system uses a quadrupole channeltron residual gas analyser (RGA) within a chamber, which is pumped by a turbomolecular drag pump. Under the control of the main control programme, samples of the module gases are leaked at regular intervals, through the controllable leak valve into the analysis chamber. Using the RGA the gas composition is computed in parts per million (ppm) of the 64 most relevant mass numbers. The analysis is corrected for offsets, background, and the mass positions. The mass spectrum is then compared with a reference gas spectrum. An acceptable tolerance on each mass number is defined for each reference spectrum. The system allows contamination of <1ppm to be detected. If a mass number falls out of the specified tolerance, an alarm message is communicated. The control of the gas checking is performed by the main matrix control program. The gas analysis is performed by a dedicated code written using a bespoke programming language designed for mass-spectrometry applications. Communication between these codes is performed through a SCADA database using dynamic data exchange (DDE). The system has been used to optimise the method of pumping and purging the matrix when changing gases. The results of tests, which have allowed the development of fast gas change cycles with little contamination or gas wastage, are presented.

3:20pm **VST-ThA5 Calibration Stability of Hot Cathode Ionization Gauges: A Discussion of the Importance of Electron Path Length and Gauge Constant***, **R.N. Peacock**,* Retired

The ion current, I, in an ionization gauge is given by the equation I = K i P where K is the gauge constant, i, the electron current, and P the pressure. Values of K for gauges designed for use at UHV and XHV range from 10/Torr to 10@super 6@/Torr. It is important to know whether calibration stability is sacrificed when K, and the electron path length, are large. Using a simple model, the electron path length is estimated as a function of the probability, @beta@, that an electron will make another pass through the ionizing region. An equation is obtained for K as a function of @beta@. The fractional change in K, @DELTA@K/K, is calculated for a 1% reduction in the probability that an electron will make another pass through the ionizing region. The fractional change is zero for those gauges where the electrons make a single pass, 0.015 for a B-A gauge with K = 25, and 0.91 for a gauge with K = 10@super 4@.

3:40pm **VST-ThA6 Calibrating Cold-Cathode Gauges at Very Low Pressures***, **B.R.F. Kendall**,* Elvac Laboratories*; E. Drubetsky,* Televac Division of the Fredericks Company

Cold-cathode ion gauges are now used in a wide range of high vacuum applications. Because of their freedom from many of the errors associated with hot-cathode gauges, they are becoming increasingly popular for use at ultra-high vacuum. Their calibration at low pressures, especially below about 10@super -9@ Torr, presents special challenges because of the rather complex (yet stable) logarithmic nature of their current-pressure response. These parameters must be established by tests at known pressures extending to the 10@super -11@ Torr range or lower. This in turn requires the use of special hot-cathode reference gauges such as the extractor, modulated Bayard-Alpert or X-ray-neutralized Bayard-Alpert types. We describe calibration procedures and results for a number of cold-cathode gauges at pressures in the 10@super -8@ to 10@super -11@ Torr ranges. Some aspects of conventional calibration techniques may be inappropriate or counterproductive at very low pressures because of X-ray, outgassing and ion desorption errors in the hot-cathode reference gauges. Preliminary results with a newly-developed cold-cathode reference gauge are discussed.

4:00pm **VST-ThA7 Residual Gas Analysis using Microengineered Systems*,* *S. Taylor,*** University of Liverpool, UK **INVITED**

There has been an increasing trend in recent years towards miniaturisation in mass spectrometry. Miniature versions of time of flight (TOF), magnetic sector and quadrupole ion trap have all been demonstrated. The use of silicon integrated circuit fabrication techniques (MEMS) has led to microengineered (submillimetre) versions of many of the more popular mass spectrometers including crossed field, travelling wave and quadrupole (QMS) instruments. In this presentation a brief survey of the various miniature systems which have been or are being developed will be given and their potential for use in residual gas analysis will be assessed. Recent results arising from the UK microengineered QMS project will also be presented and discussed. The performance and reliability of microengineered single-element quadrupole devices have both been raised considerably by improved construction methods. The mass range was raised from 50 to 150 amu, and the mass resolution was increased to 70 (measured at 10% peak height). Sensitivity was enhanced by an order of magnitude using a miniature multiplying detector. The useable pressure range has been established and modelled. Ion coupling was optimised by using software simulations (SIMION), and several different miniature ion sources have been investigated. Array-type devices containing either nine parallel quadrupoles or five independent mass filters have been developed, together with a self-aligning ion detector array. Theoretical simulations of the microengineered QMS have been undertaken by computing the trajectories of large numbers (>10,000) of ions injected into the mass filter and show that the experimental performance for a range of operating conditions may be successfully modelled.

Biomaterials
Room 134/135 - Session BI-ThP

Biomolecule and Cell Poster Session

BI-ThP1 Interactions of Dye Molecules with Poly(Propylene Imine) Dendrimer Monolayers*, S. Chen, L. Li, C. Boozer,* ***S. Jiang****,* University of Washington

Dendrimers have been regarded as interesting candidates for applications in host-guest chemistry, such as complex drug delivery agents. A fundamental understanding of guest-host interactions in dendrimers will facilitate the effort to design new-generation chemical and biological sensors based on dendrimers. In this work, we report a systematic study of interactions between a group of dye molecules and poly(propylene imine) dendrimers (PPI) tethered to carboxyl-terminated self-assembled monolayers (SAMs). Adsorption kinetics is measured by surface plasma resonance (SPR) sensors. The fifth-generation PPI dendrimers are mainly used in this work. Our results show a strong affinity of PPI-5 to Rose Bengal or erythrosine B. The strong affinity results from well matches in charge and structure between the guest and the host molecules. In addition, the effect of various factors (e.g., dendrimer generations, charges and shapes of guest molecules, and pH values and ionic strengths of liquid solutions) on adsorption will be discussed. This is the first attempt to study the adsorption of small molecules using SPR.

BI-ThP2 Protein Adsorption on Mixed Self-assembled Monolayers*,* ***L. Li****, S. Chen, C. Boozer, S. Jiang,* University of Washington

Mixed self-assembled monolayers (SAMs) of alkanethiols on Au(111) can be used to precisely control molecular-scale chemical, structural, and biological surface properties via controlling the abundance, the type, and the spatial (both normal and lateral) distribution of tail group sites. By controlling surface microenvironment, different structures and activities of immobilized proteins are expected. Here, we first report our recent studies on phase behavior of mixed alkanethiols with two compounds having different chain lengths (C8-C18) and terminal groups (-COOH, -OH, -CH@sub 3@, and -NH@sub 2@) on Au(111). These mixed SAMs are characterized by scanning tunneling microscopy (STM) and atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), contact angle measurements, and ellipsometry. Results show that closely packed and homogeneously mixed SAMs can be achieved at the molecular level. These controlled surfaces will then be used for the adsorption of various proteins such as albumin, lysozyme, etc. Adsorption behavior is characterized by tapping-mode AFM and surface plasmon resonance (SPR) sensors. Results show that molecular-scale mixed SAMs generally promote protein adsorption. The effect of the abundance, type, and spatial distribution of terminal groups on protein adsorption is explored systematically in this work. Keywords: Mixed SAMs, protein adsorption, AFM, SPR, and XPS.

BI-ThP3 Studies of Phosphopeptides on Metal Impregnated Plasma Polymer Surfaces*,* ***J. Zhang****, J.D. Whittle, H. Qiu, R.B. Timmons, G.R. Kinsel,* The University of Texas at Arlington

Surface-protein interactions play an important role in the fields of biology and medicine. Recent work in our group has focused on the binding affinity of phosphopeptides for metal ions immobilized on vinyl acetic acid modified PET substrates. Our work demonstrates that, under specific solution conditions, phosphopeptides have high binding affinities for copper. This observation has been utilized to purify / clean-up phosphopeptides on-probe before sample analysis by Matrix Assisted Laser Desorption / Ionization (MALDI) Mass Spectrometry (MS). Our initial studies focus on the development of surfaces for extraction / isolation of phosphopeptides via coordination with surface bound metal ions. PET substrates (4.8 mm diameter disks) were modified by pulsed RF plasma deposition of polymerized vinyl acetic acid. Metal ions were incorporated into the vinyl acetic acid modified PET substrates by immersion of the substrates into various metal ion solutions. Specific binding of phosphopeptides to the surface was first demonstrated by exposure of the metal impregnated film to a mixture of the peptide buccalin and the phosphopeptide p60 substrate II. Washing of the surface with the buffer MES (pH = 5.5)/10%acetonitrile led to selective removal of the buccalin peptide from the surface film. (This step was confirmed by MALDI analysis of the wash solution.) Similar methods have also been successfully applied to the extraction of phosphopeptides from alpha-casein tryptic digests. The purification of phophopeptides resulted in an increase in the peptide MALDI ion signal and improved ion signal resolution. Additional studies have focused on the effect of changes in the metal ion used for phosphopeptide binding, changes in the solutions used for washing / peptide release, and metal-ion binding of histidine-rich peptides.

BI-ThP5 Time-of-flight Secondary Ion Mass Spectrometry (ToF-SIMS) Characterization of Adsorbed Proteins with Amino Acid Mutations*,* ***N. Xia****, R. To, S.L. McArthur, P.S. Stayton, D.G. Castner,* University of Washington

Static time-of-flight secondary ion mass spectrometry (ToF-SIMS) was used to detect amino acid sequence mutations in adsorbed streptavidin. A series of mutations were introduced into wild-type streptavidin using site-directed mutagenesis. Both wild-type and mutant strepavidin were adsorbed onto polystyrene. Then positive and negative static ToF-SIMS spectra were acquired. For mutants where one amino acid (either glutamic acid or serine) in each strepavidin monomer was replaced with a cysteine the largest differences were observed in the negative spectra. The appearance of ToF-SIMS peaks at 32 (S@super -@) and 33 (HS @super -@) indicated the incorporation of cysteine into the streptavidin mutants. Only small changes in the positive ion ToF-SIMS spectra were observed upon incorporation of cysteine into streptavidin (e.g., the appearance of a small peak at 45 due to the CHS @super +@ fragment from cysteine). Introduction of a larger mutation (linking a histidine tag to the C-terminus of each streptavidin monomer) resulted in larger changes in the positive ion ToF-SIMS spectra. Due to the relative complexity of the positive spectra from proteins, principal component analysis (PCA) was used to analyze the differences in the positive spectra. The largest changes introduced by the presence of the histidine tags were observed in the intensities of the peaks at m/z=81, 82 and 110, which correspond to the primary mass fragments from the amino acid histidine.

BI-ThP7 Dynamics and Chemistry of ELISA Test for Toxins by In-situ and Ex-situ Spectroscopic Ellipsometry*,* ***D.W. Thompson****, E.M. Berberov, G.L. Pfeiffer, J.A. Woollam,* University of Nebraska-Lincoln*; T.E. Tiwald, C.M. Herzinger,* J.A. Woollam Co., Inc.*; T. Datta,* University of South Carolina

Fast, in-situ spectroscopic ellipsometry at 225 simultaneous visible wavelengths is used to study dynamics of deposition in liquid solution of each layer in a four-layer enzyme-linked immunosorbent assay (ELISA) for cholera toxin. Time-dependent functional relationships of cholera and Escherichia coli heat-labile enterotoxin attachment to monosialoganglioside (G@subM1@) coated substrates are studied, as well as the attachment of associated antibodies. Ellipsometric selectivity between toxins is demonstrated. In addition, ex-situ spectroscopic ellipsometry from vacuum-ultraviolet (131 nm / 9.5 eV) to mid-infrared (35 microns) on each constituent layer of the ELISA is studied. Several distinct oscillator-like features in the visible to vacuum-UV are found at 1.42 eV, 4.24 eV, 6.32-6.35 eV, and 10.98 eV. Protein resonant chemical oscillators in the individual layers are identified as: C-H in CH@sub2@ and CH@sub3@, N-H, O-H, and P=O, seen at 3307 cm@super-1@, 2926 cm@super-1@, 2958 cm@super-1@, 1662 cm@super-1@, 1546 cm@super-1@, 1245 cm@super-1@ and 1081 cm@super-1@. In summary, in-situ and ex-situ spectroscopic ellipsometry covering vacuum-UV to mid-infrared is a simple, nondestructive way to study dynamics and chemistry of nanometer dimension ELISA films. Research supported by NSF SBIR contract number NSF II-9901510.

BI-ThP8 Do the Chemical Properties of Polymeric Surfaces Influence the Bacterial Adhesion?*,* ***G. Speranza****, R. Canteri, C. Pederzolli, G. Gottardi, L. Pasquardini, E. Carli, M. Grosello, A. Lui, M. Anderle,* ITC-irst, Centro per la Ricerca Scientifica e Tecnologica, Italy

Understanding the mechanisms underlying the interactions between biological systems and polymeric surfaces is of paramount importance. In fact, for their physico-chemical properties, polymers as biomaterials, are utilized in a even larger variety of applications. However, an increasing significance in the medical routine is assumed by the development of bacterial infections caused by implanted polymeric devices (up to 40% of nosocomial infections). In this respect the investigation of the phenomena which take place at the interface between polymeric surface and bacterial wall, are gaining a great relevance. Due to the high level of complexity, these processes, to the best of our knowledge, are still not well clarified. Aim of this work is to investigate this topic to reach a deeper degree of comprehension. The description of the interfacial interactions at the biomaterial surface normally make use of the van der Waals forces. A new term that involves acid-base interactions is here hypothesized to fully describe the bacterial adhesion to the polymer surface. Two requirements are needed to test this hypothesis: an ideal polymeric surface in terms of chemical and morphological properties and "standard samples" as bacterial strains. Several experiments were worked out using the Escherichia Coli (Gram-) strain and its growth on polymers having an "acid" or "basic" character, was investigated. The first findings seems to indicate that the bacterial adhesion is influenced by the chemical properties of the polymeric surface. This first results may be interpreted taking into account a mechanism in which the acid/base (Lewis) interaction plays an important role.

BI-ThP9 Photoluminescent Study of Bacterial Lipid A Langmuir-Blodgett Monolayers*, **V.V. Kislyuk**, L.D. Varbanets, Z.I. Kazantseva, I.M. Pahuta, V.Z. Lozovski,* National Academy of Sciences of Ukraine, Ukraine

The photo luminescent spectra have been studied at room temperature for the Lipid A Langmuir-Blodgett monolayers grown on various substrates of Au, Si and SiO@sub 2@. The maxima of the spectral profiles are shifted towards long waves as compared to the spectra of 10@super -2@% DMSO solution and water suspension of the lipid. The energy difference of approximately 0.4 eV is, likely, attributed to the molecule-molecule and molecule-surface interaction of the monolayer. The luminescence has been stimulated with pulses of UV laser (337 nm, 100 Hz, 8 ns) or UV lines of Xe lamp and registered with photon counter with the coincidence circuit. The lipid A were extracted from the membrane of Ralstonia Solancearum.

BI-ThP10 Human Foreskin Fibroblast Cell Studies on Micropatterned Substrates Created by Selective Molecular Assembly Patterning*, **J.W. Lussi**, R. Michel, A. Goessl, M. Textor, J.A Hubbell,* Swiss Federal Institute of Technology, Switzerland

A novel patterning technique, termed "Selective Molecular Assembly Patterning" (SMAP), was used to produce cell-adhesive patches on a cell-resistant background. The method is based on selective adsorption of alkane phosphates to titanium oxide, but not silicon oxide surfaces. Using standard photolithographic techniques patterns of titanium oxide within a matrix of silicon oxide were created. A self-assembled monolayer of dodecyl phosphate (DDP) formed on the titanium oxide, while poly(-L-lysine)-poly(ethylene glycol) graft copolymer (PLL-PEG) subsequently rendered the silicon oxide matrix resistant to cell adhesion. A combination of phase contrast and fluorescent microscopy was used to examine the spreading of human foreskin fibroblast (HFF) cells seeded on the patterned substrates. Unstained cells, as well as cells stained for cytoskeletal f-actin and the focal adhesion protein vinculin, were examined. HFFs adhered only to the DDP-coated TiO2 patches, clearly recognizing the substrate pattern. The PLL-PEG coated SiO2 matrix remained completely resistant to cell adhesion in fetal bovine serum containing medium for more than 5 days. Cell surface contacts were observed on DDP-coated TiO2 patches and stress fibers traversed patterned features. Cell shape on patterned substrates differed significantly from HFF cultured on homogenously cell-adhesive substrates. Cells exhibited more angular shapes imposed by the square symmetry of the oxide pattern. Cell extensions frequently bridged several features without establishing contacts to the background surface. These cell experiments conclusively demonstrate the usefulness of this patterning method for studying cell adhesion on patterned surfaces.

BI-ThP11 Self-Assembly Approaches to Preparation of Self-Supported Porous Films for Selective Cell Separations and Tissue Engineering Scaffolds*, **M. Tanaka**, M. Miyama, K. Nishikawa, J. Nishida, M. Shimomura,* Hokkaido University, Japan

Selective cell separation is one of the most important issues in the field of tissue regenerative medicine at present. We prepared self-supported porous films of poly(@beta@caprolactone) or poly(lactic acid-co-glicolic acid) with wide range of controlled pore size (0.5-100 µm) and area (diameter 1-20 cm) to develop high-performance filters and tissue engineering scaffolds. The self-supported porous films were fabricated by a simple casting technique and self-assembly proceses@footnote 1,2@ without lithographic methods. The films had highly regular patterns and stable net structure with high mechanical stability and moderate elasticity. Creation of desirable pore size was easy, and the pore size can be controlled simply by changing the evaporation rate of the polymer solutions. The porous film which had been a novel biocompatible poly(2-methoxyethyl acrylate)@footnote 3,4@ coated was attached to a module having an inlet port and outlet port to simulate a leukocyte eliminating. The film provided the 100% selective separation of the leukocyte from human blood. The leukocyte eliminating ratio and platelet recovery were dependent on the pore structures (size and depth) and the chemical properties (hydrophilicity and surface charge). The biocompatible and biodegradable films could be expected as promising materials to produce useful selective cell separations, implants and cell-supported elastic scaffold for various medical devices. @FootnoteText@@footnote 1@N. Maruyama et al., Thin Solid Films, 327-329, 854-856 (1998) @footnote 2@T. Nishikawa et al., Mater. Sci. & Eng. C, 10, 141-146 (1999) @footnote 3@M. Tanaka et al., Biomaterials, 21, 1471-1481 (2000) @footnote 4@M. Tanaka et al., Polymer Int, 49, 1709-1713 (2000)

BI-ThP13 Analysis of Cell Organization in a Smooth Muscle Culture Grown On High Aspect Ratio Microstructures*, **J.D. Glawe**, D.K. Mills, B.K. Gale,* Louisiana Tech University

Tissue engineered organs may someday replace donated organs. The first step towards realizing this goal is to create three dimensional cell cultures that preserve the organization of cellular orientation found in tissue in vivo. One promising method of achieving this goal is to microfabricate scaffolds with microcontainers designed to allow cell growth in only one direction. This is essential for engineering muscle tissue where to remain functional, all cells must contract along the same axis. The tissue culture scaffold was specifically designed to accommodate smooth muscle cells (SMC's). It was molded out of polydimethylsiloxane (PDMS) from a lithographically patterned SU-8 structure. The structure is coated with protein to promote improved cell adhesion. Two methods of seeding the cells into the scaffold were tested, gravitational and centrifugal seeding. The microcontainers are approximately 500 µm in depth and are either square, octagonal, or plus-shaped, with varying diameters. Measurements were made to determine cell density, orientation, actin concentration, and the percent of living cells at four intervals after cell seeding.

BI-ThP14 Ion Implanted Titanium: Relating Surface Chemistry to Cellular Response.*, **F.H. Jones**, L. Shinawi, S. Nayab, I. Olsen, J.A. Hobkirk,* University College London, UK*; T.J. Tate, D.S. McPhail,* Imperial College of Science, Technology and Medicine, UK

Titanium-based materials are used extensively in hard tissue biomedical implants, often with inorganic coatings to promote bone regeneration and integration. The properties of such coatings remain less than ideal; variable composition, dissolution at low pH and fracture failure or delamination continue to present serious problems. Direct modification of the surface using ion implantation has been proposed as a possible alternative, giving a favourable interface for interaction with the host tissue, without affecting bulk properties. The homogeneity and controllability of ion implantation also mean that the technique is ideal for studying the fundamental effects of chemical composition on cellular response to a surface. Ca implantation has been shown to promote osseointegration,@footnote 1@ but little attention has been paid to the effect of the nature of the substrate on the resulting surface chemistry, or the difference in behaviour of surfaces implanted with different ions. The current work examines the effect of ion implantation into native Ti, air oxidised Ti and TiO@sub 2@ single crystals. Ca, K and Ar ions, selected due to their similar masses, were implanted at doses up to 2x10@super 17@ ions cm@super -2@. Preliminary cell culture studies indicate significant differences in cell behaviour depending on the chemical nature of the implanted ion. Of particular interest are adverse effects observed on Ar-implanted surfaces, despite the inert nature of argon. In parallel, XPS and SIMS were used to investigate surface chemistry. The effects of annealing in UHV and immersion in water were found to be element-dependent. The nature of the ion was also found to influence the interaction with model organic species in solution and the rate of calcium phosphate deposition from mineralising solutions. @FootnoteText@ @footnote 1@ Hanawa T, Kamiura Y, Yamamoto S, Kohgo T, Amemiya A, Ukai H, Murakami K, Asaoka K. J. Biomed. Mater. Res. 36 (1997) 131.

Magnetic Interfaces and Nanostructures
Room 134/135 - Session MI-ThP

Magnetic Thin Films & Surfaces Poster Session

MI-ThP1 Magnetic Spectroscopy at the Elliptically Polarizing Undulator Beamline 4.0.2 at the Advanced Light Source*, **E. Arenholz**, A.T. Young,* Advanced Light Source

Beamline 4.0.2 is the first undulator beamline at the Advanced Light Source equipped with a Sasaki-type elliptically polarizing undulator (EPU). The EPU allows full control of the polarization of the x rays. Variable linear polarization from linear horizontal to linear vertical as well as 100% circular polarization are possible. The undulator in combination with a plane-grating-variable-included-angle monochromator is designed to provide high flux photon beams from 50 eV to 2000 eV, fully covering the L@sub 3,2@ edges of important magnetic transition metals (Fe, Co, Ni, ...) and also the M@sub 5,4@ edges of magnetic rare earth elements of interest (Gd, Tb, ...). We will present first experimental results that illustrate the ability of the beamline to detect small dichroism effects in dilute systems and materials which show only weak magnetic effects (<0.3%), giving us confidence in the suitability of the set up to study novel magnetic systems with high precision.

MI-ThP2 X-ray Magnetic Linear Dichroism of Fe-Ni Alloys on Cu(111)*, **T.F. Johnson**, S. Chiang, Y. Sato,* University of California, Davis*; D.A. Arena,* Lawrence Livermore National Laboratory*; S.A. Morton,* University of Missouri-Rolla*; M. Hochstrasser, J.G. Tobin,* Lawrence Livermore National Laboratory*; J.D. Shine, J.A. Giacomo, G.E. Thayer, D.P. Land, X.D. Zhu,* University of California, Davis*; G.D. Waddill,* University of Missouri-Rolla

We have prepared Fe@subx@Ni@sub1-x@ multilayers on Cu(111) in order to learn how to control the structure and magnetism of these thin alloy films, which are relevant to the giant magnetoresistance (GMR) effect used in magnetic disk drive heads. Using the Spectromicroscopy Facility (7.0.1.2) on Undulator Beamline 7.0 at the Advanced Light Source, we have measured X-ray magnetic linear dichroism (XMLD) signals from both Fe and Ni 3p lines for fourteen different thin Ni-Fe alloy films on Cu(111), with Fe concentration ranging from 9% to 84% and for a variety of film thicknesses. The Curie temperature for all of these samples was in the range 200K to 500K. For many of these films, the Curie temperature was considerably lower than was previously seen for similar films deposited on Cu(100). For a particular Fe concentration x, the Curie temperature increases with alloy film thickness. For a specific film thickness, the Curie temperature has a maximum near x=0.4. We have also measured the Fe and Ni asymmetries as a function of Fe concentration.

MI-ThP4 Growth of Mn on Fe(001): Surface Alloy Formation and Multilayer Growth*, T. Yamada, M.M.J. Bischoff, A.J. Quinn,* University of Nijmegen, The Netherlands*; T. Mizoguchi,* Gakushuin University, Japan*; **H. van Kempen**,* University of Nijmegen, The Netherlands

A complicated relationship is usually found between the magnetic configuration of a magnetic thin film, the crystallographic structure and the electronic structure. Mn films on Fe(001) are the ultimate example of a system where all these properties are interwoven. Conflicting results are, e.g., reported on the magnetic properties, which suggest a strong dependence on impurities, intermixing, and growth mode. Scanning tunneling microscopy (STM) is the ideal technique to tackle this problem, since it allows studying both the atomic structure in the conventional constant current mode and the electronic structure in the spectroscopic mode. In this contribution, it will be shown that for deposition of submonolayers at temperature s above 400K, Mn atoms are place exchanged with Fe substrate atoms. Locally a c(2x2) MnFe surface alloy is formed. Spectroscopy measurements will be presented for incorporated Mn atoms, pure Mn islands, and the local c(2x2) MnFe alloy structures which all show characteristic features in the dI/dV spectrum. For growth of thicker Mn films at 400K, intermixed Fe atoms can still be observed until the third layer. Analysis of the step heights gives evidence that the structure relaxes after the second layer. From the fourth layer upon, spectroscopy measurements reveal a feature in the dI/dV spectrum which strength oscillates with layer thickness and therefore seems to be related with the reported antiferromagnetic coupling of the Mn layers. The spin-polarized nature of these surface states can be used to study the surface magnetism on a local scale in spin-polarized tunneling experiments. Experiments with Fe covered tungsten tips will be discussed.

MI-ThP6 Epitaxial Growth of Ferromagnetic Ni@sub 2@MnIn Thin Films on InAs (001)*, **J.Q. Xie**, J.W. Dong, J. Lu, S. McKernan, C.J. Palmstrom,* University of Minnesota

There has been growing interest in ferromagnetic/semiconductor hererostructures for the development of spintronic devices which utilize the carrier's spin as well as its charge. InAs is the semiconductor of choice because of its high electron mobility and the ease to form an ohmic contact to it. Although no elemental ferromagnet is lattice matched to InAs, the lattice mismatch between the Heusler alloy Ni@sub 2@MnIn and InAs is only 0.2%. In bulk, Ni@sub 2@MnIn is reported to have a cubic (L2@sub 1@) crystal structure with a lattice constant a@sub 0@ = 6.069 Å and a Curie temperature ~ 314 K. Recent theoretical studies showed that the minority spins are situated at the @GAMMA@ point in Ni@sub 2@MnIn and the majority spins are far away from the @GAMMA@ point. Therefore, the band structure alignment between Ni@sub 2@MnIn and InAs would enhance the injection of the minority spins, suggesting that Ni@sub 2@MnIn may be a good choice for spin injection as a ferromagnetic contact. In this talk, we report on the epitaxial growth of Ni@sub 2@MnIn thin films on InAs (001) by the molecular beam epitaxy technique. Both in situ reflection high energy electron diffraction and ex situ x-ray diffraction, Rutherford backscattering spectrometry, and transmission electron microscopy measurements indicate the high-quality epitaxial growth of Ni@sub 2@MnIn films on InAs (001). The films have a Curie temperature ~ 170 K and a saturation magnetization ~ 420 emu/cm@super 3@. The lower Curie temperature, compared to that of bulk Ni@sub 2@MnIn, is believed to result from the growth of Ni@sub 2@MnIn in the B2 structure. Composition has a dramatic effect on the Curie temperature. For Ni@sub 2@MnIn@sub 1.7@, a Curie temperature of ~ 290 K was observed. If ordered films can be grown, significantly higher Curie temperatures may be expected.

MI-ThP7 On the Origin of the Thickness-dependent Dimensional-crossover in Ultrathin Magnetic Films*, **N.A.R. Gilman**,* Penn State University*; M. Hochstrasser,* Lawrence Berkeley National Laboratory*; R. Zhang, R.F. Willis,* Penn State University

We report experimental results that show that the order parameter @beta@, which determines the long-range (spin) ordering in magnetic thin films (M=M@sub o@(1-T/Tc)@super beta@), changes abruptly due to a crossover in dimensionality at different thicknesses in Ni(100), Ni(110) and Ni(111) films. We argue that the different critical thicknesses arise from finite-size quantization energies of the (spin) excitations, which are dependent on the magnitude of associated wavevectors spanning different crystallographic directions of the fcc Fermi surface. Experimental data on nickel alloys support this view.

MI-ThP8 Fabrication of CoCrTa Magnetic Film by RF-sputtering*, **Y. Ohta**,* Fukui National College of Technology, Japan*; K. Ohashi, T. Tsumori,* Shin-Etu Chemical Co., Ltd., Japan

CoCrTa longitudinal media was prepared by sputtering onto Si substrates at substrate temperature of 523 K by RF magnetron sputtering system. The films were fabricated at the substrate temperature of 523K and Argon gas pressure of 3.5 mTorr during sputtering. The film was deposited on surface Si and glass substrates. CoCrTa thin films of several thicknesses were prepared by sputtering. The microstructures and particle size were investigated by transmission electron microscopy (TEM) and atomic force microscopy (AFM). The crystal structure was checked by X-ray diffractometry (XRD) and the magnetic properties were measured by a vibrating sample magnetometer (VSM). The underlayer thickness dependence of magnetic properties of CoCrTa deposited on Si and glass substrates were investigated. It was known that thickness of underlayer has significant influence the crystallographic texture and magnetic properties of the magnetic layer. CoCrTa layer deposited on the Si substrate revealed small size grain and smooth surface than ones deposited on the glass substrate.

MI-ThP9 Ion-beam Modification of the Physical Properties and the Structure of Fe/Si Multilayered Films*, **Y.P. Lee**, J.S. Park,* Hanyang University, Korea*; Y.V. Kudryavtsev,* Institute of Metal Physics, Ukraine*; J. Dubowik, B. Szymanski,* Institute of Molecular Physics, Poland*; J.Y. Rhee,* Hoseo University, Korea*; G.S. Chang,* Yonsei University, Korea

The influence of ion-beam mixing (IBM) on the strucure, and the magnetic, magneto-optical and optical properties of Fe/Si multilayered films (MLF) was investigated. The IBM was performed with Ar@super +@ ions of an energy of 80 keV and a dose of 1.5 X 10@super 16@ Ar@super +@/cm@super 2@. It was shown that the IBM destroys the layered structure of the MLF down to a depth of about 110 - 150 nm and leads to the formation of a new phase which is characterized to possess a perfect crystalline structure, a low coercivity and a Curie temperature of about 550 K. It is suggested that the phase formed by the IBM is a metastable Fe@sub 2@Si silicide with a B2 type of structure. An annealing of the ion-beam mixed Fe/Si MLF at 720 K destroys further the undisturbed layered structure at the bottom and also leads to a decomposition of the Fe@sub 2@Si phase into a metastable magnetically-hard Fe@sub 5@Si@sub 3@ silicide and, presumably, Fe@sub 3@Si.

MI-ThP10 Suface Magnetic Phase Diagram for a Semi-infinite Ferromagnet*, **D.P. Pappas**,* National Institute of Standards and Technology, Boulder*; A.P. Popov,* Moscow State Engineering Physics Institute, Russia, Moscow, Russia

The phase diagram for the orientation of the surface region is calculated in the parameter space defined by the surface and bulk anisotropy for semi-infinite systems and thin films. A discrete layer-by-layer approach is developed and compared to the continuum approach. We also consider the 1.5 atomic layer Fe on Gd system, and find that it is a good physical realization of the model. We find that suface magnetic canting always occurs when the magnitude of the surface anistropy is comparable with the interlayer exchange interaction.

MI-ThP11 Low Field Magnetoresistance through Grain Boundaries in Double Exchange Compounds*, D. García, **B. Alascio,*** Instituto Balseiro, Argentina

To model transport through the grain boundary of a manganite bicrystal we study the conductance of a spin chain doped with itinerant electrons which are strongly Hund coupled to the spin at each site. We induce a domain wall in the chain and propose a single site pinning mechanism. At large pinning we find that the magnetoresistance corresponds to that of two uniformly magnetized domains. Assuming uniaxial anisotropy within each grain we use the above results to calculate the magnetoresistance through the grain boundary and obtain remarkable agreement with experiment. Further, our study solves an apparent contradiction between experiments by different authors.

MI-ThP12 Formation of Barriers for Magnetic Tunneling: Ion Embedding vs Diffusion*, **S.O. Demokritov**, B.F.P. Roos, P.A. Beck, B. Hillebrands,* University Kaiserslautern, Germany

A novel type of oxidation technique, the ionized atom beam oxidation, was used to prepare ultrathin insulating aluminum oxide barriers for magnetic tunnel junctions. Thanks to high chemical reactivity of atomic oxygen combined with very low energy (30-50 eV) of the ions the oxide grows fast, homogeneous, and amorphous. The limited oxidation depth reduces the possibility of an overoxidation of the underlaying magnetic electrode. By means of in-situ techniques for monitoring the oxide growth during the oxidation, it was possible to identify two mechanisms which dominate the oxidation at different stages of the process. During the initial stage an ion embedding mechanism controls the oxidation. This mechanism describes the penetration of kinetic O-ions into the target metal layer until they are stopped on their way through the film by elastic and inelastic processes. The ions form chemical bindings with the surrounding metal atoms at their stopping place. The oxidation depth defined by this mechanism depends on the energy of the ions and reaches 1-2 nm. As the oxide layer grows, the incoming O-ions find less and less leftover metal atoms near their stopping place and a diffusion process starts to effect the oxidation. The further oxidation growth is determined by an electrical field controlled diffusion of metal and oxygen atoms. Monte-Carlo-simulations based on the developed "ion embedding with diffusion" model completely describe the formation of thin oxide barriers for magnetic tunnel junctions.

MI-ThP13 Non-monotonic Magnetic Surface Anisotropy of Epitaxial Fe Films Grown on Vicinal Substrates*, S.O. Demokritov, **M. Rickart**, J. Jorzick, B. Hillebrands,* University Kaiserslautern, Germany

The presented work is devoted to the study of the influence of atomic steps at the interface between a magnetic film and a substrate on the magnetic surface anisotropy of the film. Step induced anisotropy contributions appear because of the broken translational invariance perpendicular to the steps. The Fe films were prepared on vicinal MgO(001) substrates with Ag(001) and Au(001) buffers using a molecular beam epitaxy UHV system. Substrates with two different miscut orientations (along [100] and [110]) were used. In-situ characterization was performed by LEED, RHEED and SPM, and chemical analysis by Auger electron spectroscopy. Magnetic anisotropy contributions have been determined from the hysteresis loops and from frequencies of spin waves measured by Brillouin light scattering. In addition to the four-fold anisotropy intrinsic for (001) Fe films the vicinal films demonstrate an uniaxial anisotropy. The strength of the uniaxial anisotropy depends on the miscut angle, the miscut orientation, and the buffer material. Fe films prepared on Au buffers with the miscut orientation along the [100]-direction show an additional uniaxial anisotropy with the easy axis perpendicular to the steps. For the Fe films prepared on Au buffers with the miscut orientation along the [110]-direction a non-monotonic dependence of the anisotropy strength as a function of the miscut angle is observed: the orientation of the magnetic easy axis switches from parallel to perpendicular to the steps, crossing zero value between 1.5 and 2 degrees of the miscut angle. Fe films prepared on Ag buffers with the miscut orientation along the [100] direction shows the same orientation of the uniaxial anisotropy easy axis, as those prepared on Au, however the anisotropy strength is much higher than that observed on Fe/Au system. The properties of the observed uniaxial anisotropies are analyzed on the basis of the Neel pair-bonding model.

Microelectromechanical Systems (MEMS)
Room 134/135 - Session MM-ThP

Poster Session

MM-ThP1 Determination of the Young's Modulus and Residual Stress in 3C-SiC Films Using the Load-Deflection Technique*, J. Mitchell, **C.A. Zorman**, M. Mehregany,* Case Western Reserve University

Silicon Carbide is an attractive mechanical material for MEMS due to its high Young's modulus coupled with its high temperature stability and chemical inertness. SiC is also receiving attention as a material for NEMS for these same reasons. The cubic polytype (3C-SiC) can be epitaxially grown on (100)Si substrates, thus providing an excellent opportunity for measuring the mechanical properties of SiC, since test structures can be fabricated using conventional Si bulk micromachining techniques. Using an interferometric load-deflection technique applied to bulk micromachined diaphragms, we have measured the spatial distribution of the Young's modulus and residual stress of 3C-SiC films grown on large-area (100 mm-dia.)(100) Si wafers. In addition to the spatial distribution, the run-to-run variation and the variation as a function of film thickness were also characterized. In general, we found that the Young's modulus, which averaged about 360 GPa, is insensitive to location on the wafer as well as film thickness. This is in stark contrast to the residual stress, which varied by as much as 200 MPa across a 100 mm-diameter wafer, and is, in general, higher for thinner films. This paper will detail the film growth process, and test sample preparation procedure, the testing technique, and the test results for 3C-SiC film thicknesses ranging from 0.125 to 2 microns. Issues pertaining to making measurements of high modulus films such as SiC using the load-deflection technique will also be discussed.

MM-ThP2 A Trench Etching Technique Using MERIE to Fabricate MEMS Accelerometers*, **K.-W. Kok**,* National University of Singapore, TEMIC Automotive (Singapore) Pte Limited, Singapore*; W.J. Yoo,* National University of Singapore

Plasma etching is an important process to form deep high aspect ratio beams in fabrication of MEMS devices. Properties pertaining to the anisotropic trench etching process have been studied using SiF4/HBr/NF3/HeO2 gas mixtures by a magnetically enhanced reactive ion etcher (MERIE). We investigated the taper angle and etching rate in the trenches, the dependency of the etching rates on pattern-size and open area ratio, and roughness on the sidewall. The etching masks of SiO2 and Si3N4 were used. In these conditions, etching selectivities of the silicon substrate with respect to the etching mask were in the range of 60 to 120 for the SiO2 mask and these were about three times higher than for the Si3N4 mask. The high etching selectivities from the SiO2 mask resulted in the steep trench profile and this made possible to form the deep trench structures of the aspect ratio of 25. Furthermore, the open area ratio on the wafer was varied in the range of 10% to 50% to determine loading effects which are problematic in inductively coupled plasma (ICP) etching. Etching rates and their uniformity across the wafer in the ICP were known to be strongly affected by the open area ratio. We found that, in the MERIE, the etching rates remained constant and their uniformity was less than 2% regardless of the open area ratio for the all pattern sizes investigated. The surface roughness on the sidewall was maintained within 5nm after deep trench etching up to 20mm, and the electrical test proved that this was acceptable to control capacitance of the MEMS accelerometers accurately.

MM-ThP3 Micro-fabrication of a Novel n-channel Field Effect Transistor Cantilever to Sense Charge Traps*, **M.S. Suh**, G.H. Yon,* Seoul National University, Korea*; Y. Kuk,* Seoul National University, Korea, South Korea

We have micro-fabricated a novel n-channel field effect transistor (FET) cantilever that is proposed to sense surface potential profile in nanometer scale. Conventional techniques used in surface and bulk micro-electromechanical system (MEMS) and combined complementary metal oxide semiconductor (CMOS) process have been employed to make a novel n-channel FET cantilever made of silicon on insulator (SOI) wafers. The cantilevers with various beam lengths, width, and thickness have been fabricated and their resonance frequencies were measured. Thermal annealing after high-dose ion implantation controlled the channel length between the source and the drain. This cantilever resembles nchannel metal oxide semiconductor FET (n-MOSFET) without a gate electrode. If a biased or charged sample is positioned closed to the cantilever, it works as the gate electrode. The device characteristics of the novel FET cantilevers were similar to the conventional n-MOSFET.

Nanometer Structures
Room 134/135 - Session NS-ThP
Poster Session

NS-ThP1 Manipulation of Organic Monolayers Confined in Molecule Corrals*, **A. Schnieders**, T.P. Beebe, Jr.,* University of Utah

Nanometer-scale organic surface structures have significant potential applications, e. g. in the field of nanoelectronics. Therefore the characterization but also the controlled production of these structures is of increasing importance. In recent years, it has been shown that scanning tunneling microscopy (STM) is, besides its wide use in the characterization of organic monolayers, also well suited for manipulation of these layers. In this study we investigate the possibility to use molecule corrals to confine the effects of manipulation of organic monolayers to small areas. Molecule corrals are nanometer-sized etch pits in the basal plane of highly ordered pyrolytic graphite (HOPG). They are formed by heating HOPG to 650° C in air. This technique produces corrals, which are uniformly circular and one monolayer deep. The radius is easily controlled by the etching time. Molecule corrals have previously been used to contain and study small numbers of molecules in their interiors and as highly controllable surface defects on graphite. We used a home build STM and a commercial STM (Multimode Nanoscope, Digital Instruments) for both, manipulation and characterization of self-organized organic monolayers on HOPG, with and without molecule corrals. Most of the experiments were performed under a liquid droplet of the organic compound in solution at room temperature. In this presentation, we will show, among others, results on diacetylene monolayers.

NS-ThP2 Bistability in Scanning Tunneling Spectroscopy of Ga-Terminated Si(111)*, **I.B. Altfeder**, D. Chen,* Rowland Institute for Science

Demonstration of a Tunable Bistable Tunnel Device with a Low Temperature STM and A Self-organized Ga Array on Si(111)@footnote 1@ Bistable electron transport, a phenomenon usually associated with double-barrier structures, has been observed with a conventional STM junction formed between a metal tip and a Ga-terminated Si(111) surface at 77 K. Large hysteresis loops appear in the current-voltage characteristics when electrons are injected from the tip to the surface. The turn-on bias varies from -3.1 to -4.0 V and shows an inverse dependence on the tip-sample distance, indicating a strong field effect. The turn-off bias, however, is essentially pinned at a conductance threshold of -2.7 V.

NS-ThP3 Nanostructures of Si Luminescence Materials Fabricated by Microwave Plasma CVD*, H. Kezuka,* Tokyo University of Technology, Japan*; **I. Kato**, T. Matsumoto, R. Saito,* Waseda University, Japan*; T. Suzuki,* Tokai University, Japan

The double-tubed coaxial line-type microwave plasma CVD(Chemical Vapor Deposition) system has been developed for obtaining a stable plasma with a low gas pressure in order to fabricate electro-microdevices and photonic devices. In this paper, the microwave plasma CVD is applied for the fabrication of nano-particles of a-Si:H. In this system, the microwave power is confined in the the cavity, and not injected into the plasma in the chamber. Thus,in the deposition chamber,the gas flow forms spatial afterglow plasma with no microwave power injected. He outer discharge tube is composed of fused quartz and the inner tube is made of stainless steel. The Ar gas is fed to the outer discharge tube and the SiH4 gas is fed to to the inner tube.The Ar gas is ionized in the cylindrical cavity region by the microwave power. The SiH4 gas flows into the Ar plasma at the discharge tube end through the inner tube, and then the SiH4 is dissorciated by the microwave power.The substrate table area is 40cm2 and is placed at z = 10 cm. The Ar gas flow rate is 110 ml/min and the SiH4 gas flow rate is 30 ml/mi.After heat-treatments of 72 hrs in air for as-deposited a-Si:H partiles, it is assumed that nano-particles(nanoball) of a-Si:H include nano-crystal(nc) Si characterized from XPS-spectrum of the oxygen 1s region and of the silicon 2p region.From SEM- and AFM-observation of the oxidized surface of nano-particles, the size of nanoballs of a-Si:H is about 20-30nm in diameter.

NS-ThP4 Si Stems Produced by Annealing Au/Si(111) Surface*, T. Takami,* Visionarts Research*; **I. Kusunoki**,* Tohoku University, Japan

Nano-tubes, fibers, and wires are interested as an intelligent material supporting the "nano-technology". Silicon nano-wire@footnote 1@ and other semiconductor nano-wires@footnote 2@,@footnote 3@ had already been produced before the discovery of carbon nano-tube by Iijima.@footnote 4@ Recently, Homma et al.@footnote 5@ succeeded to form Si nano-columns on a Si substrate arranged with Au-islands by using vapor-liquid-solid (VLS) reaction of disilane (Si@sub 2@H@sub 6@). In the present work, we have demonstrated the formation of the Si stem (a bundle of nano-fibers) without using VLS reaction. Small Si particles for the seeds of the Si stems were scattered on a Si(111) wafer. After introducing the wafer in an ultrahigh vacuum (UHV) chamber, monolayer-equivalent Au atoms were deposited on the wafer by the vacuum evaporation. After the deposition, the wafer was annealed at 1000°C for 260 minutes. Then the Si stems were formed on the Si surface, which were observed by scanning electron microscope (SEM). The stems looked like tiny mushrooms in micro-meter scale. The Au atoms worked as a catalyst for the stem formation by inducing the surface segregation of the bulk-materials. @FootnoteText@ @footnote 1@ R.S. Wagner, W.C. Ellis, Appl. Phys. Lett. 4 (1964) 89. @footnote 2@ G.A. Boostma, H.J. Gassen, J. Cryst. Growth. 10 (1971) 223. @footnote 3@ E.I. Givargizov, J. Cryst. Growth. 32 (1975) 20. @footnote 4@ S. Iijima, Nature 354 (1991) 56. @footnote 5@ Y. Homma, P. Finnie, T. Ogino, H. Urisu, J. Appl. Phys. 86 (1999) 3083.

NS-ThP5 A Simple Method of Forming Small Gold Particles on a Thin Gold Film*, **M. Xiao**,* CCMC-UNAM, Mexico

We have produced gold particles whose sizes range from several tenth nanometers up to about one micrometer. The small gold particles are distributed on a gold thin film of thickness $50\sim 80$\AA. The method for the formation is simple. We first evaporated the gold thin film, and then applied DC field along the film. When the field increases from zero to 30 V, and the measured current increases from 0 to 650 mA, the particles were formed. The sizes and the distribution distances could be controlled by the applied DC field.

NS-ThP6 Theoretical Studies on One-dimensional Photonic Band-gap Structures*, M. Xiao,* CCMC-UNAM, Mexico*; **D. Soto Puebla**,* CIFUS and CICESE, Mexico*; F. Ramos Mendieta,* CIFUS, Mexico

We present numerical results of dispersion relations and transmission spectra for one-dimensional photonic band-gap structures composed of periodic metallic thin films separated by dielectric layers. In the calculation, both published experimental data and the Drude model are used to obtain the refraction index of the silver film. Influences fo various parameters on the quality of the band-gap structures are discussed on the base of the results.

NS-ThP7 CdS Self-assambled Nanostructures Produced by Pulsed Laser Deposition@footnote 1@*, C. Manzano, R. Castro,* Cinvestav-IPN, México*; J.L. Peña,* CICATA-IPN, México*; M.A. Santana-Aranda,* Cinvestav-IPN, México, Mexico*; **M. Meléndez-Lira**,* Cinvestav-IPN, México

Low-dimensional structures are very attractive due to their potential application in the production of high-efficiency opto-electronic devices. Until now, most of the semiconductor self-assembled nanostructures (SSN) have been fabricated employing epitaxial deposition techniques. The formation mechanism of SSN has been identified as the misfit strain involved during the heteroepitaxial growth. We report results of the production, and optical and structural characterization of CdS nanostructures deposited by pulsed laser deposition on Corning glass substrates (CGS), two possible mechanisms for the production of these nanostructures are discussed: 1) stress due to differences in the thermal expansion coefficients of the CdS film and CGS; 2) CdS droplets ejected from the target and directly deposited on the CGS. The samples were grown using a Nd:YAG laser focused on a rotating CdS target. Depositions were performed with 50 lasers shots employing substrate temperatures of 250, 350 and 500°C under a pressure of 10@super -6@ Torr. The morphology of the deposited CdS layers was examined by atomic force microscopy finding the presence of elliptic islands with typical dimensions around 60 and 30 nm for the major and minor axis lengths, respectively. There is no evidence of degradation with time or handling. A clear blue shift, with values up to 100 meV, of the absorption band edge was observed in the room temperature transmission spectroscopy (TS) measurements, and was attributed to quantum confinement. Room temperature modulated transmission spectroscopy (MTS) measurements indicated a blue shift of only 7 meV. The differences between the results from TS and MTS are discussed taking in account the islands size distribution. These results are correlated with those obtained from 10 K photoluminescence, x-ray diffraction and scanning electron microscopy measurements. @FootnoteText@ @footnote 1@ Work partially supported by CONACyT-México.

NS-ThP8 Atomistic Simulation Studies of Stresses and Grain Boundaries by Cu Nanowire Deformations*, **J.W. Kang**, H.-J. Hwang,* Chung-Ang University, Korea

We investigated mechanical properties of Cu nanowires with grain boundary by various mechanical deformations using classical molecular dynamics simulation. We simulated the cases of elongation, shearing, rotation, rotated elongation, and compression. Before the first yielding, nanowires preserve the elastic stages, and after this, the mechanical deformation proceeds in alternating quasi-elastic and yielding stages. For Cu nanowires with grain boundary, most of the slip events occurred in the interfaces of grain boundary. For Cu {100} nanowires in this work, all slips occurred in the [110] directions on the {111} planes. In compression case, whole nanowires region, which has originally {100} planes, was transformed into {111} planes during temporary state. However, in other cases, such as elongation, [100] shear, [110] shear, and rotation, only part of nanowires region were transformed into {111} planes.

NS-ThP9 Micro-Fabrication of Sub-wavelength-Size Aperture for Near-Field Optical Probe*, **M.Y. Jung**, J.W. Kim, D.W. Kim, S.S. Choi,* Sun Moon University, Korea

There have been considerable interests about the microfabrication of the submicron size hole due to the potential application of the near field optical sensor array for gigabyte storage device. We have previously reported fabrication of the submicronsize oxide aperture.@footnote 1@ In this report, the 5 micron size dots were photo-lithographically patterned on the Si (100) wafer. After formation of the V-groove shape utilized by anisotropic KOH etching, the orientation dependent oxide growth was performed to have an etch-mask for dry etching. The reactive ion Cl2 etching using inductively coupled plasma (ICP) system will be performed in order to etch thin SiO2 layer on the bottom of the etch stop and to etch the Si on the bottom. After etching, the fabricated submicron-size oxide aperture followed by a proper metal deposition and silicon nitirde deposition procedures can be utilized as a near field optical probe. @FootnoteText@@footnote 1@Seong S. Choi, J.W. Lee, J.W. Kim, M.Y. Jung, D.W. Kim, American Physical Society Meeting, G32.011, March 21, 2000, Minneapolis, MN. USA.

NS-ThP11 An Apparatus for Deposition of Size-selected Clusters and Fabrication of Cluster-assembled Films*, **N. Tarras-Wahlberg**, M. Andersson, A. Rosén,* Chalmers Univ. of Tech. and Göteborg Univ., Sweden

We present the design of an apparatus for deposition of size-selected metal clusters. The clusters are fabricated in a laser vaporization source. It consists of a cavity where pulsed light from a Nd:YAG or excimer laser vaporizes metal atoms into a continuous flow of He atoms at a pressure of 10 - 50 mbar and clusters are formed. The cluster-buffer gas mixture exits the cavity through a nozzle (0.5 - 1 mm diameter) and the beam passes a differential pumping stage until it reaches the vacuum chambers for characterization and deposition. At several positions along the cluster beam quartz crystal microbalances and Faraday cups can be inserted to measure the total mass and ion yields. In the first vacuum chamber, just outside the nozzle the deposition rate is high, e.g. 4 Å/s of non size-selected Fe-clusters at 10 Hz repetition rate. A time-of-flight mass spectrometer is used to monitor the cluster production and to characterize the cluster size distribution, and a quadrupole mass filter will be used for size selection and deposition of monodisperse clusters. In previous deposition experiments we have made iron cluster films on HOPG and characterized their magnetic properties [C. Johansson et al., Nanostr. Mater. 12 (1999) 287].

NS-ThP13 Gas-Phase Purification of Single-Wall Carbon Nanotubes using H@sub 2@S and O@sub 2@ Mixture*, **T. Jeong**,* LG Innotek, Korea*; Y.B. Hahn,* Chonbuk National University, Korea

A purification process combining both a gas-phase purification using H@sub 2@S and O@sub 2@ mixture to remove impurity carbon particles and an acid treatment to remove metal particles has been developed for single-wall carbon nanotubes (SWNTs), synthesized by an arc-discharge method. Acid solution of 3 M HCl was used to remove catalyst metal particles out of the as-grown SNWTs. Thermal oxidation using the H@sub 2@S-O@sub 2@ gas mixture was followed to preferentially remove unwanted carbon particles. Hydrogen sulfide played a role of enhancing the removal of carbon particles as well as controlling the oxidation rate of oxygen with carbon. The optimum gas ratio was 10 ml H@sub 2@S/min and 20 ml O@sub 2@/min. After the acid treatment and thermal oxidation at 500 °C for 1 h, we achieved carbon nanotubes purity of > 90 % with yield of 20 - 50 %, depending on the purity of starting material.

NS-ThP14 Growth of Spherical Diamond Tips on Small Cylindrical Substrates*, V. Baranauskas, **A.C. Peterlevitz**, H.J. Ceragioli, S.F. Durrant,* Faculdade de Engenharia Eletrica e Computacao - UNICAMP, Brazil

This work demonstrates the possibility of growing spherical diamond tips on the top of metallic rods using chemical vapor deposition (CVD). Spherical diamond tips are of interest for diverse applications, including micro-drilling tools, waveguides, field-emission devices, biomedical instruments and so on. A hot-filament CVD system fed with ethanol highly diluted in hydrogen was used. The nucleation and growth parameters for such spherical diamond tips differ from those for deposition on flat surfaces since there is no competition for space between the neighboring grains to growth in their preferred crystalline direction, which often results in columnar structured materials on flat surfaces. A model for scaling-down or scaling-up the diameter of the diamond tips will be presented. Morphological data obtained by scanning electron microscopy (SEM) and results of Raman spectroscopic analyses of the samples produced with different diameters are discussed.

NS-ThP15 The Carbonitride Nanostructures Synthesized by Microwave Plasma Enhanced Chemical Vapor Deposition in an Acetylene / Ammonia Plasma System*, **S.-H. Lai**, K.-H. Hong, H.C. Shih,* National Tsing Hua University, Taiwan

The carbonitride nanostructures consisting of nanotubes and nanofibers have been synthesized on Pd-coated porous silica by microwave plasma enhanced chemical vapor deposition (MPECVD) at a temperature of about 600°C and the precursors are H@sub2@, C@sub2@H@sub2@, NH@sub3@, and N@sub@2. The condition of Pd clusters was varied with the power density and the bias to the substrate during the plasma immersion ion implantation (PIII) process. Samples were analyzed by SEM, HRTEM, EELS, and XPS. It was found that carbonitride nanostructures are strongly affected by the surface morphology of the Pd implant layer and the N content. HRTEM and EELS studies showed that the degree of linearity and graphitization of the nanostructure decreases as the N content increases. Nevertheless, the field emission properties of the nanostructures are enhanced due to the N doping. Form the XPS results, N is either bonded to two C atoms (sp@super2@ pyridine-like type) or to three (sp@super3@ bridgehead-nitrogen type) in the hexagonal sheets.

NS-ThP16 STM Observation of Nanoscale Defects Formed by Annealing the 6H-SiC Surface*, **M. Yoshimura**, K. Ojima, K. Ueda,* Toyota Technological Institute, Japan

It was recently reported that the carbon nanotube can be produced on the SiC surface by annealing at high temperature around 1800K. Carbon-terminated surface is considered to be more appropriate for the growth of nanotube than the Si-terminated surface. The transimission electron microscopy (TEM) has been utilized to investigate the growth mechanism for both surfaces. However the determination of the precise atomic structure, such as the location of the pentagons and defects, is difficult only by TEM observation. Here we demonstrate scanning tunneling microscopy (STM) study of the elucidation of Si-terminated SiC surface by annealing. A commercially available 6H-SiC wafer (CREE) was used as a specimen. It was annealed up to 2000K in UHV. STM observation was performed at room temperature with a tungsten tip. After annealing at 1600K, following defect structures were observed on the flat graphite layer; (1)Protruded particles with 4-5nm in diameter were observed and its surface showed /3x/3 superstructure. (2) Nanotube-like structures lie on the surface. They are probably formed by rolling of a graphite layer from the step. (3) Star-shaped defects of 3nm size were frequently observed. The surrounding graphite area also shows the /3x/3 superstructure. The surface was then annealed to 2000K, however, the surface structure was basically unchanged and no nanotube formation normal to the surface was detected. We discuss detailed structure of the defects and its formation mechanism.

NS-ThP17 Scanning Spreading Resistance Microscopy of MOCVD Grown InP and GaAs Optoelectronic and Microelectronic Structures*, **St.J. Dixon-Warren**, G. Pakulski, A.J. SpringThorpe, G. Hillier, D. Macquistan, R. Streater,* Nortel Networks, Canada*; R.P. Lu,* Simon Fraser University*; K.L. Kavanagh,* Simon Fraser University, Canada

Scanning spreading resistance microscopy (SSRM) is a new scanning probe microscopy technique that provides localized resistance profiling over a semiconductor surface. The technique, which is based on contact-mode atomic force microscopy (AFM), provides information on the two dimensional distribution of charge carriers and on the position of pn junctions in semiconductor structures. We have used SSRM to examine the cleaved edge of a number of MOCVD grown InP and GaAs optoelectronic and microelectronic structures, such as heterojunction bipolar transistors and buried heterojunction laser structures. We have also performed careful measurements on dopant staircase structures. Information on the spatial distribution of dopants in the epitaxial layers was obtained, and the effect of the applied tip voltage was investigated. We will also compare the SSRM results with those obtained using Scanning Capacitance Microscopy (SCM) on the same samples. Finally, we plan to report preliminary results for SSRM and SCM measurements for devices under operating bias conditions.

**NS-ThP18 Active Feedback Noise Cancellation Low Temperature Scanning Tunneling Spectroscopy*, D. Chen*, *S.L. Pryadkin,* The Rowland Institute for Science*; B. Wang, H. Wang,* University of Science and Technology of China

A scanning tunneling microscope (STM) is one of the most sensitive mechanical and acoustical noise sensors. This in turn makes it difficult to perform fine resolution spectroscopy. Here, we describe a novel UHV and low temperature (4.2K) STM consisting of two tips which can be actuated independently. In the spectroscopy mode, one of the tips serves as the noise sensor whose signal is phase inverted and fed to the second tip to lock the tip-to-sample separation during an I-V measurement. This active feedback method effectively improves the signal-to-noise ratio. More importantly, under the low thermal drift conditions, such as in low temperature operation, it allows the long-time averaging of the measurement while avoiding artifacts due to residual mechanical instability of STM. Examples o the tunneling electron spectroscopy performed on quantized nano-structure will be demonstrated.

Organic Films and Devices
Room 134/135 - Session OF+SS-ThP
Molecular Aspects of Organic Films Poster Session

OF+SS-ThP1 In-situ Characterization of Photoisomerization Process and Thermal Stability of Highly Photoreactive SAMs on Gold with PM-IRRAS*, T. Wei,* National Institute of Advanced Industrial Science and Technology (AIST), Japan*; K. Tamada,* AIST and Frontier Research System, RIKEN, Japan*; H. Akiyama, K. Yase,* AIST, Japan*; S. Kim,* Hanyang University, Korea

In this paper, we discuss conformational change of photoreactive azobenzene SAMs composed of unsymmetrical disulfides on Au(111)/mica under UV/Vis photoirradiation, by use of polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS). Two different azobenzene dyes are utilized in this study; One is a conventional azobenzene unit, and another is a "CH3-attached azobenzene" unit, in which methyl group is introduced to the azobenzene ring to avoid dye aggregation sterically. The "CH3-attached azobenzene" SAM exhibited the stronger nas-CH2 peak at higher frequency position compared with the conventional azobenzene SAM, sugesting more disordered film structures due to the methyl group. For in situ observation of photoisomerization reaction, we performed PM-IRRAS measurements under irradiation of 365nm UV light for cis, and 440nm Vis light for trans. For both unsymmetrical disulfide SAMs, with conventional azobenzene unit (C6AzSSC12) and with "CH3-attached azobenzene" unit (C6Az(Me)SSC12), the intensities of n(benzene ring) and nas (c-o-ph) vibration modes clearly decreased after UV irradiation, as a evidence of photo-isomerization reaction taking place. These IR spectrum changes by photoirradiation were not detected for azobenzene thiol SAMs. After annealing in oven at 100°C for three hours, the IR spectra of both disulfides (C6AzSSC12, C6Az(Me)SSC12) changed to the direction of more disordered or tilted chains, however, the change of C6Az(Me)SSC12 is rather larger than that of C6AzSSC12. These results were compared with our SPR and AFM data for thermal stability.

OF+SS-ThP3 Scanning Tunneling Microscopy Investigation of the Self-Assembly of Photochromic Molecules on Au(111)*, T. Fritz,* ***S. Mannsfeld,*** *T.W. Canzler,* TU Dresden, Institut fuer Angewandte Photophysik, Germany*; S. Stumpf, K. Gloe,* TU Dresden, Institut fuer Anorganische Chemie, Germany*; K. Leo,* TU Dresden, Institut fuer Angewandte Photophysik, Germany

The self-organization of photochromic molecules on Au(111) surfaces has been investigated by Scanning Tunneling Microscopy (STM). Self-assembly films of the organic molecule 6-[4-(phenylazo)phenoxy]hexane-1-thiol (AzoC@sub 6@) have been prepared by immersion of epitaxial gold films on mica in ethanolic solutions (1mmol) for 24 h up to 72 h. High-resolution STM images, using a NanoScope III in air, reveal the ordered growth of AzoC@sub 6@ in several domains, typically 20 nm in size. A detailed structural analysis was performed on drift-corrected images. In contrast to literature results where a so-called bundle model was suggested which can hardly explain the growth of rather extended domains, we will show evidence that a molecular lattice is formed which is commensurate with the Au(111) surface lattice. The two-dimensional unit cell contains two AzoC@sub 6@ molecules. All experimental findings are compared to theoretical calculations, based on a geometric lattice match algorithm.

OF+SS-ThP4 On the Relation between Experimental Vibrational Spectra and Spectra Determined from Ab Initio Calculations: Small Organic Molecules on Single Crystal Metal Surfaces*, P. Uvdal,* *M.P. Andersson,* Lund University, Sweden*; A.D. MacKerell, Jr.,* University of Maryland

Using small organic molecules, alkoxies and pyridine, adsorbed on single crystal metal surfaces we show that a detailed understanding of the vibrational spectra is possible with the aide of ab initio electronic structure calculations. Specifically we investigate on an ab initio level the surface induced alteration of (a) isotopic shifts (b) intramolecular coupling and (c) Fermi resonance coupling between binary modes and fundamentals. The experimental data is obtained in UHV using a FTIR spectrometer.

OF+SS-ThP5 Surface Plasmon Resonance Techniques for In Situ Detection of LCST Behavior on Surface-Grafted Polymer Films*, S. Mendez,* *S. Balamurugan, L.K. Ista, G.P. Lopez,* University of New Mexico

Thin films of the temperature responsive polymer, poly(N-isopropylacrylamide) (PNIPAAM), were polymerized in situ on azo-initiator derivatized self-assembled monolayers (SAMs). Carboxylic acid and methyl-terminated alkanethiols were used to form mixed component SAMs on gold substrates. Reaction of the COOH moieties with Woodwards reagent K and an amine containing azo-initiator resulted in immobilization of the initiator on the surface. PNIPAAM was then grown from the surface upon exposure of the surfaces to heat and monomer solution. Varying the concentration of COOH-thiolate within the original SAM allowed us to control the surface coverage of the polymer. Surface plasmon resonance (SPR) was used to detect the lower critical solubility temperature (LCST) transition of these surface-grafted polymers by taking advantage of a difference in both thickness and refractive index of the polymers in their relaxed (low temperature) and collapsed (high temperature) states. Realtime, in situ reflectance measurements of the PNIPAAM films immersed in water were taken as the temperature of the samples was raised. The effect of surface coverage on the position and degree of the transition was also examined.

Organic Films and Devices
Room 134/135 - Session OF+TF-ThP
Aspects of Organic Films Poster Session

OF+TF-ThP2 Tuning Supramolecular Self-assembly of Trimesic Acid Molecules on Cu(100) by Copper Adatoms*, A. Dmitriev,* ***N. Lin,*** *J. Weckesser,* Max-Planck-Institut for Solid State Physics, Germany*; J.V. Barth,* EPFL, Switzerland*; K. Kern,* Max-Planck-Institut for Solid State Physics, Germany and EPFL, Switzerland

Recently, it was reported that one-dimensional supramolecular nanostructures can be realized via intermolecular hydrogen bonding.@footnote 1@ Here we demonstrate that, for the system trimesic acid (TMA) on Cu(100), one can tune the intermolecular hydrogen bonding by adjusting the density and mobility of Cu adatoms and hence fabricate various supramolecular nanostructures. In our experiments submonolayers of TMA on Cu(100) have been prepared by organic molecular beam epitaxy (OMBE) under ultrahigh vacuum and in situ characterized by scanning tunneling microscopy (STM). The TMA molecules are parallel to the surface (flat-lying) as deposited and form hydrogen-bonded chicken-wire networks via dimerization of their carboxylic acid groups.@footnote 2@ These networks are only stable at low-temperatures (< 250 K) and at room-temperature rapidly transform into a stripe-like structure, where the TMA molecules are perpendicular to the surface (up-standing). By means of CO predosing, Cu coevaporation or adjustment of the substrate temperature the Cu adatom density and mobility have been controlled, which allows to convert the hydrogen bonded carboxylic acid dimers into copper-carboxylate complexes.@footnote 3@ Sequences of STM images directly demonstrate the real time formation and dissociation of single chemical bonds in copper-coordinated supermolecules. Cu adatoms of high density and mobility finally leads to well-ordered two-dimensional supramolecular nanostructures of large domain size on the surface. @FootnoteText@ @footnote 1@ J.V. Barth, J. Weckesser, C. Cai, P. Gunter, L. Bargi, O. Jeandupeux and K. Kern (2000) Angew. Chem. Int. Ed. 39, 1230-1234 (Angew. Chem. 112, 1285-1288). @footnote 2@ S.V. Kolotuchin, P.A.

Thiessen, E.E. Fenlon, S.R. Wilson, C.J. Loweth and S.C. Zimmerman (1999) Chem. Eur. J. 5 No. 9, 2537-2547. @footnote 3@ C.C. Perry, S. Haq, B.G. Frederick and N.V. Richardson (1998) Surf. Sci. 409, 512-520. .

OF+TF-ThP3 Current Response of Nickel Phthalocyanine Ozone Sensing Films Formed by Plasma-activated Evaporation, ***S. Takeda,*** Takushoku University, Japan

Nickel phthalocyanine(NiPc) sensing films for O@sub 3@ gas have been fabricated by r.f.- plasma-activated evaporation and common vacuum deposition techniques. Sensor structure as a detecting element has a inter digital type Au or Pt electrode deposited on a glass substrate. Sensing NiPc films formed on the electrode are about 400 and 800 Å in thickness. Original value of electric resistance of the NiPc films between the electrodes is about 10@super -10@-10@super -11@ @ohm@ , but exposing the sensing film to O@sub 3@ gas it immediately changes down to 5-6 order of magnitude under the applied voltage d.c.1.5 V. Response time of the current corresponding to 63% of the saturated value (time constant 1 @tau@) is about 3.5 min. Due to more thinner NiPc films response time can be shorten and saturate more quickly. In this report we showed the data of only with 150 ppm but this kind of sensors can be detectable it more lower than 5 ppm. From the results of response characteristics, it suggests that absorbed O@sub 3@ gases on the NiPc film diffuse inside the film, so that the response time of cause, depends on the film thickness and structure. Comparing the response times with 400 and 800 Å, thinner one is shorter several times than the other, and also the films prepared by plasma-activated evaporation respond quickly than that the films without plasma-activation. To clarify the reason of different responses, morphologic images of the NiPc films were observed by Atomic Force Microscope. Surface of the films formed by common vacuum deposition is likely needle crystals but the other films show very flatness.

OF+TF-ThP4 Mobility, Binding Transition and Ordering of C@sub 60@ on Pd(110): Investigations at the Local and Mesoscopic Scale, ***J. Weckesser,*** Max-Planck-Institut fuer Festkoerperforschung, Germany*; C. Cepek,* Laboratorio Nazionale TASC-INFM, Italy*; R. Fasel,* Swiss Federal Laboratories for Materials Testing and Research, Switzerland*; J.V. Barth,* Ecole Polytechnique Federale de Lausanne, Switzerland*; T. Greber, J. Osterwalder,* Universitaet Zuerich, Switzerland*; K. Kern,* Max-Planck-Institut fuer Festkoerperforschung, Germany

We present a comprehensive study of C@sub 60@ on a Pd(110) surface using scanning tunneling microscopy (STM), low-eneregy electron diffraction (LEED), x-ray photoelectron spectroscopy and diffraction (XPS and XPD). The mobility and interactions of C@sub 60@ on a Pd(110) surface have been characterized by variable temperature scanning tunneling microscopy. The motion of isolated C@sub 60@ molecules was directly monitored and the corresponding tracer diffusion barrier was determined to (1.4±0.2) eV. Upon annealing to 700 K the C@sub 60@ molecules undergoe an irreversible bonding transition resulting in a second, more strongly bound C@sub 60@ species. This is associated with a local substrate reconstruction whereupon C@sub 60@ molecules sink into the formed microscopic pits. The rearrangement of Pd substrate atoms turns out to play a crucial role similarly in the formation of C@sub 60@ thin films. In STM three well-ordered structures consisting of alternating dark and bright molecular rows are found, in combination with LEED and XPS their real space structures are determined. The height difference in STM is attributed to a local reconstruction of the Pd substrate. Whereas the C@sub 60@ molecules of the bright molecular rows are adsorbed in one layer deep microscopic pits, C@sub 60@ accommodated in two layer deep pits account for the dark molecular rows. XPD results complete the understanding of the film structure and reveal the orientation of the C@sub 60@ cages.

OF+TF-ThP7 In-situ Synthesis of Self-assembled Polyaniline/ Poly(styrene sulfonic acid) Composite Ultra Thin Films, ***T. Koga,*** *H. Otsuka, A. Takahara,* Kyushu University, Japan

In-situ preparation method of self-assembled polyaniline (PANI)/ poly(styrene sulfonic acid) (PSS) composite ultra thin films on aminosilane grafted surfaces was proposed. PSS was adsorbed onto the aminosilane grafted Si-wafers, then PANI/ PSS composite ultra thin films were prepared in-situ by template polymerization utilizing ionic interaction between PSS and aniline. PANI/ PSS composite ultra thin films were characterized by time of flight secondary ion mass spectroscopy (TOF-SIMS), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and ultraviolet-visible-near infrared (UV-Vis-near IR) spectroscopy. Composition of PANI/ PSS composite ultra thin films estimated by XPS gave good agreement with the calculated value based on the chemical structures. AFM images and UV-Vis-near IR spectra revealed that the progress of conjugation of PANI/ PSS composite ultra thin films. From these results, it can be inferred that the formation of ultra thin films is closely related to the electrostatic character of functionalized substrate surfaces. In this method, PSS plays an important role as a template for polymerization of aniline. Therefore, the positively charged surfaces facilitated the formation.

OF+TF-ThP8 Growth and Nucleation of 2-methyl-4-nitroaniline (MNA), ***K. Nam,*** *K.I. Seo, L. Wang, C.E. Bonner,* Norfolk State University*; E.S. Gillman,* Jefferson Lab

Despite the intense interest in the microstructure of MNA over the last decade, a detailed understanding of its structure with respect to growth conditions is still not clear. A relationship between structure and growth of thin films is often sought, however in many instances these relations are vague and complex. One reason is that thin film properties generally vary by orders of magnitudes depending upon preparation conditions. Thin films are, in general, not ideal materials systems in terms of bond distortion, coordination, point defects, dislocations, compositional inhomogeneities and impurities, grain boundaries and disordered low-density void regions. These defects are created by a complex array of parameters that are directly related to the surface interface. Thus, it is expected that any quantitative description of preparation-property relations must first start with a quantitative description of its internal and external morphology. Here we present results for MNA thin films that are grown using an organic molecular beam deposition (OMBD) technique.

OF+TF-ThP9 The Dielectric Properties of P(VDF-TrFE) Copolymer Thin Films by Physical Vapor Deposition, ***G.B. Park,*** Yuhan College, Korea*; M.Y. Chung, J.H. Yoon,* Inha University, Korea*; S.H. Park,* Unix Electric Co. Ltd, Korea*; S.H. Lee,* Korea Institute of Industrial Technology, Korea*; D.C. Lee,* Inha University, Korea

The copolymer thin films of poly(vinylidene fluoride-trifluoroethylene), which shows excellent piezoelectricity and pyroelectricity, were fabricated by physical vapor deposition method in the compositions 70/30 and 80/20 mol%. The effect of the substrate temperature and the mol% rates on the molecular structure, the dielectric and piezoelectric properties was investigated. In deposition process, the substrate temperature(Ts) was varied from 30°C to the Curie transition temperature(Tc). From the results of deposition rate, molecular and crystal structure of the films, it was found that 300°C was the optimal evaporation temperature in the process. The @beta@-form characteristic peaks increased with increasing the substrate temperature on account of the increase of the crystallinity, but over 90°C the peaks decreased according to the phase transition from the ferroelectric crystal phase to the paraelectric crystal phase. From this results, the copolymer films were fabricated from 30°C to 90°C substrate temperature. The relative dielectric constant decreased as a form of anomalous dispersion with increasing measurement frequency. With increasing Ts, the relative dielectric constant increased from 3.643 to 5.29 on the 70/30mol% films, and from 4.367 to 10.77 on the 80/20mol% films, respectively. The @alpha@ relaxation by interfacial polarization and the @beta@ relaxation by dipole orientation polarization were observed in low and high frequency region, respectively. The @alpha@ relaxation decreased and the @beta@ relaxation increased with increasing Ts. From the results, it is suggested that the crystallinity of the films increased with increasing Ts. The effect of increasing Ts on the piezoelectric properties will also be discussed in detail.

OF+TF-ThP11 Optical Characterization of ZnO-CdO Thin Films Grown by Sol-Gel Method, ***T. Hata,*** *H. Komaki,* Miyazaki University, Japan

Wide bandgap oxide-semiconductors have attracted much attention for liquid crystal displays and solar cells. Recently, ZnO based materials are much respected for UV light-emitting devices. ZnO is a semiconductor with a large bandgap of 3.4 eV and a large excitonic binding energy of 60 meV. CdO is an also semiconductor with a direct bandgap of 2.3 eV and small indirect bandgap of 0.8 - 1.1 eV. The bandgap energy can be changed from 2.3 to 3.4 eV on ZnO and CdO mixed crystal. Moreover, although CdO is known to have a poor optical transmittance in the visible spectral region in comparison with those of ZnO films, CdO thin films are enough to be used for the window material for solar cells. Pure ZnO and CdO films have been studied many research groups. However, ZnCdO films have been few studied previously.In this work, ZnO-CdO thin films were grown by sol-gel dip coat method on glass and Silicon (Si) substrates at 100 ~ 600 °C under air atmosphere. The sol-gel technique is known to have the distinct advantages of process simplicity, lower cost and ease of composition control. Precursor solutions of ZnO-CdO are prepared by dissolving both 5 wt.% zinc acetate dihydrate and 5 wt.% cadmium acetate dihydrate into anhydrous ethanol for the solutions to have the desired Cd/Zn at.%. Poly-ZnO and -CdO thin films are obtained on the glass substrate more than 500 ¡C and 200 °C, respectively. A value of full width at half maximum of (100) peak at the XRD spectra become small with the increasing the growth temperature. By using the Si substrate (100) instead of the glass substrate, poly-ZnO and -CdO thin films have (100) orientation. Moreover, an optical transmittance and bandgap energy of the Zn@sub X@Cd@sub 1-X@O thin films decrease nonlinearly with the decreasing X values.

OF+TF-ThP12 XPS Study of Conducting Polymer Film Growth on Si(111) by Electrochemical Deposition Method*, H. Kato,* ***S. Takemura,*** Kanto Gakuin University, Japan

Electochemically deposited conducting polymer polythiophene (PT) films on Si(111) were investigated by XPS. PT/Si(111) interface at the initial stage of electrochemical polymer growth was closely investigated by analyzing the core-level energies and spect ral profiles of the atomic components. Spectral profiles of Si core-level spectra showed that both Si 2s and 2p spectra were basically composed of different three Gaussian components correspond to different valence states of Si in contrast to the core-lev el spectra of non-deposited Si(111). The lower peaks (LS1 and LS2) observed in Si 2p spectra of PT/Si correspond to the Si states with strong interaction between Si and PT. The peak height of LS1 slightly increases and LS2 drastically grows in the case of PT polymer growth on Si substrate. The C 1s core-level spectrum was composed of a higher energy component and a lower energy component originated from the polymer backbone and oxidized Si layers, respectively. Affinity between a deposited polymer PT film and Si substrate was strong compared with the case of a PT film deposited on ITO substrate expecting bondings between polymer chains and Si substrate layers.

OF+TF-ThP13 XPS Studies of Conducting Polymer Hybrid Films Incorporated with Dye Molecules*,* ***H. Kato****, S. Takemura, N. Aragaki,* Kanto Gakuin University, Japan

Conducting polymer polythiophene (PT) films incorporated with dye molecule safranine T (ST) prepared by electrochemical doping and diffuse injection methods were investigated by XPS. Polymeric structure, charge transfer and interaction between dye molecul e and PT backbone in the hybrid films were closely investigated by analyzing the core-level energies and spectral profiles of the atomic components. XPS core-level analysis of N 1s showed that dye molecules were injected into polymer matrix in hybrid fil ms. In the case of PT film incorporated with ST, drastic change of C 1s, S 2p, and Cl 2p core-level spectra between electrochemically as-grown and reduced films was observed. In the case of electrochemically reduced sample core-level energies of C1s and S 2p were shifted to the lower energy side indicating the creation of n-type polymer chain while in the case of electrochemically as-grown sample the polymer chain is p-type. The splitting of S 2p reflects the strong interaction betwen ST molecule and PT backbone. The C 1s core-level spectrum varied with the degree of electrochemical reduction. The C 1s spectrum is basically composed of two different Gaussian components. In the highly reduced case lower energy component grows while in the low reduced case higher energy component becomes dominant. The spectral change reflects the existence of different charged states in polymer backbone.

OF+TF-ThP14 Surface Freezing and Self-ordering Phenomena of Long Chain n-Alkanes Studied by Newly Developed High Vacuum DTA Apparatus*,* ***Y. Ouchi,*** Nagoya University, Japan*; Y. Yamamoto,* Nagoya Institute of Technology, Japan*; M. Kuroi, N. Yamaguchi, H. Ishii, K. Seki,* Nagoya University, Japan

We developed a new apparatus of differential thermal analysis (DTA) capable of simultaneous measurement of UPS, XPS, NEXAFS etc to investigate phase transitions of ultra-thin films of organic molecular systems. The apparatus is installed in a high vacuum chamber for thermal isolation and measurements of photoelectron emission. The performance of the apparatus was examined using a 650 Å-thick pentacontane (n-C@sub 50@H@sub 102@) film, which may exhibit a unique monolayer phase transition at air (vacuum)/liquid interface, known as a surface freezing self-organization effect. We observed two anomalies of DTA curve around the bulk melting temperature, one of which is apparently due to thebulk melting. Since the temperature dependence of the surface specific UV photoemission measurements showed corresponding changes in photoemission current, we could conclude that the other phase transition peak originates from the formation of frozen (crystallized) single molecular layer located at the top alkane liquid surface. We will report the detailed analysis on the transition entropy and the chain length dependence of the temperature region of the existence of this unique surface freezing layer up to n=72. Though it was believed from grazing X-ray reflection measurements that the effect will disappear around n=60, our DTA system could confirm their existence over n=60. This demonstrates that our DTA apparatus is sufficiently sensitive to examine the 2D phase transitions of monolayers. Simultaneous measurement with other photoelectron emission measurement will be beneficial for the investigation of temperature dependence of organic thin films and its self-organization process.

OF+TF-ThP15 Comparison of Alkyl-phosphonic Acid (APA) and Alkyl-carboxylic Acid (ACA) Self Assembled Monolayers on the Hydrated Alumina Surface of Aluminium*,* ***T.A. Lewington,*** UMIST, UK, U.K*; G.E. Thompson, M.R. Alexander,* UMIST, UK*; E. McAlpine,* Alcan International, UK

The interaction of organics with metal oxide surfaces is important in many areas including corrosion protection and adhesion promotion. Good corrosion protection has been obtained using APA SAMs deposited on Al prior to painting.@footnote 1@ The phosphonic acid head-group interacts with the surface of alumina to form a phosphonate bond.@footnote 2@ It is presumed that resin components react with the phosphonic acid tail-group when di-functional molecules are used. Detailed characterisation of ACAs on Al has been reported but not of APAs.@footnote 3@ The formation of alkyl-thiol SAMs on Au has been extensively studied.@footnote 4@ In contrast to the stable Au metal surface Al forms an oxide, the outer region of which is readily hydrated on exposure to ambient conditions. Two approaches have been employed to obtain reproducible Al surface chemistry for self-assembly: solution pre-treatment or atmospheric exposure. Here, SAMs have been formed on sputtered Al by immersion in 5 mM ACA and APA solutions in n-hexadecane and ethanol respectively. Surface pre-treatment with acetic or methyl-phosphonic acid was compared with 24 h atmospheric exposure. Both XPS and contact angle measurement of SAMs on Al indicate relationships between assembly, time and alkyl chain length similar to alkyl-thiols on Au. Notable differences include changes in the oxide surface, found by XPS to occur in ethanoic solutions, and the importance of pre-treatment. FTIR provides information on the orientation of the SAM and the bonding to the surface. This enables a model of the APA-Al system to be proposed, which may be compared with existing models of ACA-Al. The electrochemical properties of uncoated SAMs are investigated using cyclic voltammetry and rationalised in terms of the models. @FootnoteText@ @footnote 1@I Meage et al. Prog Org Coat 34(1998)1 @footnote 2@RD Ramsier et al. Surf Sci 203(1998)72 @footnote 3@DL Allara, RG Nuzzo Langmuir 1(1985)52 @footnote 4@GM Whitesides, PE Laibinis Langmuir 6(1990)87.

OF+TF-ThP17 Giant Polarization in Organic Heterostructures*,* ***T.U. Kampen****, I. Thurzo, D.R.T. Zahn,* TU Chemnitz, Germany

Deep levels or polarization effects can influence the charge transport through organic layers. Both effects can be identified by charge deep-level transient spectroscopy (Q-DLTS). Here, deep levels or polarization effects cause the charge transient signal Q(t) to be dependent or independent on the bias voltage, respectively. Q-DLTS, accompanied by feedback charge capacitance (FCM) measurements, has been used in the present work to investigate an organic heterostructure grown on an inorganic semiconductor. GaAs(100) substrates (n = 0.3 4x10@super 18@ cm@super -3@) were sulfur passivated by wet chemical etching and additional annealing under ultra-high vacuum (UHV) conditions. Organic molecular beam deposition was used for the growth of 20 nm of 3,4,9,10-Perylenetetracarboxylic dianhydride (PTCDA, Lancaster) and 27 nm of tris-(8-hydroxyquinoline) aluminum (Alq3, Syntec). Silver was evaporated on the Alq3 film through a shadow mask resulting in an array of circular contacts with an area of A = 2.1x10@super -7@ m@super 2@. The back contact to the GaAs(100) was achieved by an In-Ga-alloy resulting in a series resistance of less than 20@OMEGA@. The electrical characterisations were done at room temperature and in situ in the UHV system. The Q-DLTS measurements show a well resolved maximum in Q(t). The amplitude remains almost constant as a function of the bias voltage, which is a clear indication of a polarization in the organic heterostructure. From the experimental results the permittivity dispersion is determined to 2.37. The permittivity dispersion is independently obtained from FCM measurements. With the experimentally determined excess capacitance @DELTA@C of 90 pF and the thickness of the organic heterostructure the permittivity dispersion is determined to 2.42. The FCM scans show no hysteresis due to the absence of deep levels. The @DELTA@C/C = 1 presented here clearly indicates the presence of a giant polarization.

Photonics Materials Topical Conference
Room 134/135 - Session PH-ThP

Poster Session

PH-ThP1 Photoconductivity Perculiarities of @gamma@- Irradiated Silicon, Doped with Sulfur in Spectral Region 10,6 MCM*, A.V Karimov,* *R.Sh. Avezov,* Academy of Sciences of Republic Uzbekistan, Uzbekistan*; V.T. Tulanov,* National University of Uzbekistan named after M.Uilugbek, Uzbekistan

@gamma@-irradiation influence on Si < s > photoconductivity in spectral region 10,6 mcm was investigated. It was found that while compensation degree was increased both dark and light resistivities increased by 3-4 orders. Photoconductivity of sulfur doped silicon in the region of 10,6 mcm was investigated very poor. We know only one work,@footnote 1@ fulfilled under photoreciever cooling up to 5 K. The purpose of this paper is to investigate @gamma@-irradiation influence on Si ~~photoconductivity under cooling up to liquid nitrogen temperature. It is known that under @gamma@ -irradiation of silicon a number of donor and acceptor levels are created in the gap.@footnote 2@ As donor levels are placed in the lower half of the gap and sulfur creates a number of donor levels in the upper part of the gap, they don't reveal themselves in 10,6 mcm photoconductivity. Only acceptor levels have influence, decreasing the filling of donor levels created by sulfur and free electrons concentration in conductivity band. The samples were investigated with specific resistivity 80 @OMEGA@.cm., produced by sulfur diffusion into crucileless p-type silicon with initial specific resistance 1600 @OMEGA@.cm. Samples were of parallelogram form with dimensions 10 x 8 x 1 mm@super 3@. Two nickel contacts were drifted electrochemically on one side of greater area at 7mm apart from one another. As irradiation source there was used impulsive CO@sub 2@ laser LGI-50, that gives impulse of 150 mcs duration and 13 mJ energy. Direct voltage 10 V was applied to the sample. Dark current value and photoresponse were measured by memorizing oscillograph S8-12. As @gamma@-irradiation source there was used @super 60@Co, that created flux 1,7·10@super 12@ quanta/cm@super 2@·s. Kinetic equation for one level model (but with several values of energetic levels) was solved and it was established that no less than two energetic levels in semiconductor's gap take part in 10,6 mcm photoconductivity. @FootnoteText@ @footnote 1@ N. Sclar. Infrared Physics. 1976, V.16, P.435 @footnote 2@ V.C. Vavilov, I.P. Kekelidze and L.S. Smirnov. Influence of radiations on the semiconductors. M. Nauka, 1988.~~

PH-ThP2 Using the Ultrasound Treatment for Grain Boundary Passivation and Improvement of Multi-Si Recombination Properties*, A.V Karimov,* Academy of Sciences of Republic Uzbekistan, Uzbekistan*; **Kh. Ismailov,** Sh.N. Bahronov,* Academy of Sciences of Republic Uzbekistan

The photoconverters (PC) has been produced on the base of n and p type multicrystalline silicon with the thickness of 250-300 µm. The technological route of PC included the chemical and mechanical treatments of the wafers (cutting, chemical and mechanical polishing, chemical cleaning and drying), p-n junction was formed by boron thermal diffusion (T~1000-1070 °C) or phosphorous (T~930-970 °C) those penetrated to 0.4-0.7 µm from the solid state reused target. The multi-layer system Ti-Ni-Cu has been used as a collector. The annealing of contacts was carried out at T~ 540-600 °C. The contact frontal topology has been chosen as one- and two-sided grid with the collector buss width of 1mm and contact grid - 0.2 mm. The distance between strips was 3mm. The silicon monoxide (d~ 1000 A) and dioxide SnO@sub 2@ layers were formed by CVD method. This layers were used as antireflection coatings. The total PC area was ~2 cm@super 2@. The samples have been used to study the influence of ultrasonic treatment. The samples have been put into bath with ethanol. On the bottom of the bath was placed the ultrasonic wave sensor (CTS-19). Generator G3-41 with controllable output power exited it. For our case 2.5 MHz frequency and 1 W/cm@super 2@ power were used. The exposure time was chosen experimentally, all measurement was carried out at room temperature. Study of the spectral characteristic of solar cells based on multicrystalline Si under the ultrasonic treatment shown the significant dependence on the exposure time. For example, the 40 minutes exposure leads to photosensitivity increasing. The following increasing of the exposure time up to 120 minutes caused reducing of the photosensitivity on 10-15 %. The spectral characteristics in short-wave spectral range are changed substantially compared to long-wave range. The voltage-current characteristics behave analogously, but they demonstrate the increasing of open circuit voltage (~5%). The dependence of short circuit current on the exposure time in the USW is qualitative agreed with the photocurrent spectral dependence. Totally the changing of the solar cell parameters can be connected with series resistance, and with changing of the material parameters.

Plasma Science
Room 134/135 - Session PS-ThP

Plasma Etching Poster Session

PS-ThP1 Damage Recovery of Etched PZT Thin Films in CF@sub 4@/Cl@sub 2@ Plasma with the Addition of Ar, N@sub 2@ and O@sub 2@*, **M.G. Kang**, K.T. Kim, C.I. Kim,* Chung-Ang University, Korea

Ferroelctric lead zirconate titanate (Pb(Zr,Ti)O@sub 3@) thin films have been known for their applications in memory devices such as nonvolatile ferroelecric random access memory (FRAM) because of their high dielectric constants and bistable polarization. It is expected that PZT will improve the limitations in storage density encountered in conventional Si memory technology. Among the various dry etching techniques, great attention has been paid to the reactive ion etching (RIE) because it provides a high degree of anisotropy and good selectivity with the great process control. However, the RIE process degrades electrical properties, which are related to physical damage and chemical residue contamination. In this study, PZT thin films were etched by additive Ar, N@sub 2@, O@sub 2@ in CF@sub 4@/Cl@sub 2@ inductively coupled plasma. The etch rate is observed by various parameters. We also observed the effect of etching damage in PZT thin films during etching in inductively coupled plasma (ICP) etching system. SEM is used to survey the etching profile. We investigate that the recovery characteristics of etching damage used rapid thermal annealing (RTA) at various temperature. The polarization-electric field (P-E) curves were measured with a RT66A ferroelectric tester. The physical damages to the near surface of PZT are evaluated by atomic force microscopy (AFM) and x-ray diffraction (XRD) The etched surface was surveyed x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS) analysis. This research was supported by the Consortium of Semiconductor Advanced Research (COSAR) as project No. 00-B6-C0-00-09-00-01

PS-ThP2 Dry Etching Characteristics of YMnO@sub 3@ Thin Films Using Inductive Coupled CF@sub 4@/Cl@sub 2@/Ar Plasma*, **C.I. Kim**, D.P. Kim,* Chung-Ang University, Korea

Ferroelectric YMnO@sub 3@ thin films are excellent dielectric materials for high integrated ferroelectric random access memory (FRAM). YMnO@sub 3@ thin films have one polarization axis (c-axis), contain heavy and hard-deoxidizing elements, and do not contain volatile elements such as Bi and Pb, which easily diffuse into the Si substrate and lead to point defects. In this study, YMnO@sub 3@ thin films were etched with a CF@sub 4@/Cl@sub 2@/Ar gas combination in inductively coupled plasma (ICP). Etching characteristics on ferroelectric YMnO@sub 3@ thin films have been investigated in terms of etch rate and selectivity. The CF@sub 4@/(CF@sub 4@+Ar) was fixed at 0.2, and the YMnO@sub 3@ thin films were etched by adding Cl@sub 2@. Etching properties of YMnO@sub 3@ were measured according to the various etching parameters such as the rf power, dc-bias voltage, chamber pressure, and gas mixing ratio. The chemical reaction in the surface of the etched YMnO@sub 3@ films was investigated with x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). For the diagnosis of the CF@sub 4@/Cl@sub 2@/Ar plasma, optical emission spectroscopy (OES) and Langmuir probe were used. The etch profile and surface residues of etched YMnO@sub 3@ thin films was investigated by scanning electron microscopy (SEM). @FootnoteText@ Acknowledgement; University Research Program supported by Ministry of Information and Communication in South Korea.

PS-ThP3 Reduction of Plasma-Induced Damage through Ion-Ion Synchronous Bias*, **L.J. Overzet**, S.K. Kanakasabapathy,* University of Texas at Dallas*; K.P. Cheung, M.V. Malyshev,* Agere Systems

Electron-shading induced differential-charging of anisotropic etch structures has been shown to be a cause of plasma process induced-damage.@footnote 1@ It is due to a disparity in the angular velocity distributions of negative and positive species in conventional electron-ion plasmas. Electron-free plasmas, also known as negative-ion/positive-ion (ion-ion) plasmas can be made devoid of this disparity. The comparable masses and average energies of negative and positive ions in the center of an ion-ion glow allow nearly equal anisotropy to be produced in their velocity distributions when biased. Ion-ion plasmas can be formed by extinguishing the plasma power and waiting an appropriate time. For example: electrons are lost rapidly (~10's of µsec) to attachment in the afterglow of pulsed Cl@sub 2@ discharges leaving behind an ion-ion plasma that lasts for ~100's of µsec. Alternating fluxes of high kinetic energy positive-ions and negative-ions can then be produced by applying a low-frequency AC bias to the processing substrate. When this AC bias is pulsed synchronously with the plasma power and phase locked to the ion-ion plasma, it can produce alternating fluxes of positive-ions (Cl@sub 2@@super +@) and negative-ions (Cl@super -@).@footnote 2@ This ion-ion `synchronous bias' is superior for extracting negative-ions compared to an `asynchronous bias' due to the low DC self-bias it induces. We have demonstrated a reduction in electron-shading induced potentials for ion-ion synchronous bias using in-situ charge-monitoring circuitry. We have also compared some cross-sectional micrographs of etched polysilicon lines on oxide. Our limited results indicated an improvement in etch profiles for ion-ion synchronous bias at the smallest linewidth of 0.45µm. @FootnoteText@ @footnote 1@ G.S. Hwang and K.P. Giapis J. Appl. Phys., 82, 566(1997) @footnote 2@ S.K. Kanakasabapathy, L.J. Overzet, V. Midha and D.J. Economou, Appl. Phys. Lett., 78, 22(2001).

PS-ThP4 Investigation of Nitride Morphology after Self-Aligned Contact Etch*, **D. Keil**, J.W. Shon, B.A. Helmer, T. Chien, P. Gopaladasu,* Lam Research Corporation*; J. Kim,* Samsung Corporation, Korea*; H. Hwang,* NASA Ames Research Center

Self-Aligned Contact (SAC) etch has emerged as a key enabling technology for the fabrication of very large-scale memory devices. However, this is also a very challenging technology to implement from an etch viewpoint. The issues that arise range from poor oxide etch selectivity to nitride to problems with post etch nitride surface morphology. Unfortunately, the mechanisms that drive nitride loss and surface behavior remain poorly understood. Using a simple langumuir site balance model, SAC nitride etch simulations have been performed and compared to actual etched results. This approach permits the study of various etch mechanisms that may play a role in determining nitride loss and surface morphology. Particle trajectories and fluxes are computed using Monte-Carlo techniques and initial data obtained from double Langmuir probe measurements. Etched surface advancement is implemented using a shock tracking algorithm. Sticking coefficients and etch yields are adjusted to obtain the best agreement between actual etched results and simulated profiles.

PS-ThP5 Development of Self-aligned Contact Technology on a Capacitively Coupled System*, **T. Chien**, C. Nelson, D. Keil, E.A. Hudson, K. Makhratechev,* Lam Research Corporation

Self-aligned contact (SAC) technology was developed to enable efficient reduction of active areas of an integrated circuit. However, implementation of SAC etch and process integration has been very challenging. Many factors are known to influence SAC etch performance. This work addresses the effects of the machine factors (pressure, gas flow/ratio, temperature, RF powers, other gas addition, etc.) and different fluorocarbon gases in a capacitively coupled plasma etch system. Results from several designed experiments (DOE's) will be present which explore main effects and interactions for several key variables affecting SAC etch. Trends identified include critical dependencies of etch results on power and gas flow. To better understand the mechanisms responsible for the trends observed, UV absorption spectroscopy and Langmuir probe measurements were also implemented for each DOE condition. Correlations observed between these measurements and etch trends will be discussed.

PS-ThP6 Surface Analysis of a High Selective Polysilicon to Oxide Plasma Etching Process*, **T. Tai**, S. Molis, W. Yan,* IBM, SRDC

With continuing reduction of minimum feature size in semiconductor device fabrication, limited gate stack height becomes necessary to control the bitline?wordline capacitance, and to reduce bitline contact aspect ratio for better process performance. Tungsten, which has a lower sheet resistance and hence the capability to reduce gate stack height, has been selected to replace widely used tungsten silicide in the gate structure. However; because of the chemical nature of tungsten, tungsten to oxide RIE selectivity in the Fluorine etching enviroment is not adequate to prevent thin gate oxide (less than 40A) to be punched through. A polysilicon etch step with adequate selectivity to oxide has been developed to prevent gate oxide punchthrough. Xray Photoelectron spectroscopy and Time-of-Flight Secondary Ion mass spectrometry were applied to investigate the Poly and Oxides in a high-density plasma etching environments with HBr/Cl2/O2 chemistry. The results will lead to the undertanding of the RIE chemistry that provide the selectivity.

PS-ThP7 Investigation of the Performance of MERIE Etcher for Extended Conditions of Consumable Upper Electrode/Gas Distribution Plate Lifetime*, **D.V. Semach**,* Silicon Manufacturing Partners Pte. Ltd., Singapore

Lifetime of consumable parts used in semiconductor industry correlates directly with cost-of-ownership and overall equipment effectiveness. In this study lifetime of Bush upper electrode that is the consumable part of TEL85DRM dielectric etch chamber had been improved from conventional 500 to 1200 RF hours. The part is produced of aluminum, anodized and equipped with inserts gas holes been drilled through. During processing gas holes are enlarged because of the inserts material etching hence the gas distribution pattern conductance is increased. Continuously monitoring equipment and process parameters (process gases partial pressure, particle count, etch rate, non-uniformity, etching profile, etc.) subject to the gas holes integrated size there had been found that the pattern conductance increasing up to 400 % (during the part operation from 500 to 1200 RF hours) and even by 40 times (as a result of special inserts boring) had not affected these parameters. It proves that the pattern conductance is not a limitation factor for the chamber performance and plasma is stable and uniform under these conditions. As is well known, during running and wet clean the surfaces of the chamber parts deteriorate progressively. Series of chemical analysis of polymeric stratums been peeled out from the electrode surface had shown significant increase of AL and O level at the stratum side being in contact with the surface with increasing of the part operational time. However surface analysis of wafers been processed after the chamber wet clean and seasoning had not disclosed any AL and the other metal contaminations as at the initial stage as at 1200 RF hours of the part operation. All the results had been confirmed for several electrodes and chambers. The real possibility to extend the part lifetime to 2000 RF hours and more if apply soft wet clean method detailed in the body has also been shown.

PS-ThP8 Electron-Temperature Control in 915 MHz ECR Plasma*, **N. Itagaki**,* Kyushu University, Japan*; S. Kawakami, N. Ishii,* Tokyo Electron Co. Ltd., Japan*; Y. Kawai,* Kyushu University, Japan

In semiconductor processing, it is required to control the electron temperature in plasma for progress of microelectronic devices and minimization of substrate damage. Since the reactive processes occurred strongly depend on the electron temperature, this control is also necessary to find the best conditions for various plasma processings. An electron cyclotron resonance (ECR) plasma source has attracted much attention for its high electron density (10@super 17@-10@super 18@ m@super -3@) that can be achieved at low gas pressure (10@super -4@-10@super -3@ Torr). However, in a conventional ECR plasma produced by 2.45 GHz microwave, the electron temperature is relatively high, and it is quite hard to control the electron temperature in a wide range. Recently, we succeeded in production of a low-electron-temperature ECR plasma with high electron density using 915 MHz microwave. Furthermore, it was found that the electron temperature depends on the external conditions such as incident microwave power, gas pressure and magnetic field configuration. In this report, we measured the electron temperature of 915 MHz ECR plasma in detail and attempted to control the electron temperature by changing the external conditions. As a result, it was found that the electron temperature of the 915 MHz ECR plasma can be easily controlled by changing the incident microwave power in the case that the magnetic field configuration is flat. Especially, at the gas pressure of 8.5 mTorr, the electron temperature decreased nearly from 7 eV to 1.6 eV as the microwave power was decreased from 2.5 kW to 0.5 kW. In addition, we have tried to investigate the mechanism of a low-electron-temperature plasma production with 915 MHz microwave by measuring the spatial profile of the plasma parameters and wave patterns.

PS-ThP9 High Performance SiO@sub 2@ Etching using C@sub 4@F@sub8@ and C@sub 5@F@sub8@*, **S.H. Rha**, D. You, C.W. Lee, J.Y. Choi,* Advanced Technology Line, Korea

SiO@sub 2@ etching characteristics of C@sub 4@F@sub 8@ and C@sub 5@F@sub 8@ were comparatively studied. The 2MHz rf-biased electrostatic chuck in13.56MHz high-density transformer coupled plasma (TCP) reactor was used. The typical operating conditions is 10-15 mTorr, 300-400 sccm(total flow rate), 2500W Source power and 1800W rf-bias power. C@sub 4@F@sub 8@ and C@sub 5@F@sub 8@ were employed as source gases to investigate their differences in etching performance and selectivity on both SiO@sub 2@ and PR. For increasing the SiO@sub 2@/PR Selectivity. The CH@sub 2@F@sub 2@ was used. And the optimum CH@sub 2@F@sub 2@ mixing ratio for SiO2 etching is reported that. Based on these results, in sub-micron contact hole(0.1-1µm) etching, we achieved SiO@sub 2@ etch rate is more than 6000A and SiO@sub 2@/PR selectivity is 5:1.

PS-ThP10 Applicability of a Hollow-electrode Plasma Jet System for Etching of Diamond-like Carbon (DLC) Films*, **P.E. Lima**, H.S. Maciel, M. Massi,* Instituto Tecnologico de Aeronautica - ITA, Brazil*; R.D. Mansano,* LSI - Escola Politecnica - USP, Brazil*; G. Petraconi, W. Urruchi, C. Otani,* Instituto Tecnologico de Aeronautica - ITA, Brazil

Partly in response to the challenges of etching high-aspect-ratio features, it is introduced a new plasma tool based on the hollow-electrode discharge. Plasma jets are capable of operating at relatively low gas pressures, 10@super -5@ Torr, what is in somehow advantageous in comparison with reactive ion etching (RIE) systems, because it reduces contamination from sputtered electrode materials, which eventually produces undesirable micromasks. On the other hand, the non-uniformity of the etching with plasma jets limits the applicability of this technique for microelectronic purposes. To minimize this problem, a plasma beam formed by a multi hollow-electrode system was developed in order to produce an uniform beam, which was used to etch diamond-like carbon (DLC) films. These films of approximately 1.5 µm thick were deposited on 3-inch diameter, p-type, (100) silicon wafers, by magnetron sputtering, at a deposition rate of approximately 4.5 nm/min. After being characterized, samples were separated in two batches, one of then was etched in a single hollow-electrode plasma jet and the other one was etched in a multi hollow-electrode plasma jet. During the etch processes a mechanical mask was used to cover part of the samples with the purpose of producing a step between the etched and non-etched regions. This step was measured by a perfilometer and the etch rates were determined in different positions on the samples. The results obtained with the single configuration showed a high non-uniformity in the etching. This non-uniformity was substantially reduced by using the multi hollow cathode system. The multi hollow-electrode plasma beam system revealed to be a reliable technique for DLC films processing, giving etching uniformity and etching rate characteristics as good as those obtained with usual RIE systems, with the advantage of being a simple and low cost equipment.

PS-ThP11 Influence of Polymerization on Pressure Control System Performance during Dielectric Etch Processes*, **D.V. Semach**,* Silicon Manufacturing Partners Pte. Ltd., Singapore

Various effects taking place in plasma etch systems exert essential influence upon process characteristics and control. In this study pressure control valve (PCV) operation during dielectric etch processes in MERIE (magnetically enhanced reactive ion etching) reactor was investigated. Growth of polymers on grating type baffle separating plasma and exhaust zones of the reactor is causing the exhaust conductance and in this connection chamber pressure to change dynamically. During running of an evaluated process based on increased gas flow of high-molecular fluorocarbon and argon mixture fast changes in PCV behavior were observed. Intensive polymerization was suspected to be a main reason for these changes. Detailed monitoring of chamber manometer and PCV readings let to evaluate polymers rates of growth and shrinkage and dynamics of some other processes affecting the valve movement, and also define the limitations for pressure control. The polymers formed on anodized aluminum chamber parts were found to be thick, very dense and hard. Detailed examinations of the polymeric stratums showed that they consisted of many thin layers. The thickness of one layer was just about a hundred nanometers. Thus we could suppose that every single layer of formed polymer refers to individual wafer. Chemical analysis of the polymers showed that they consist mostly of fluorine and carbon. Ratio of fluorine to carbon contents was about 2 to 1. The investigation results show that polymers formed during plasma etching may significantly decrease pumping and pressure control systems capability depending on temperature, structure, density and volume of the polymers. Process pressure, mass flow of gas mixture components and correlation between RF power on and RF power off time intervals were found to be the main factors responsible for polymers formation and behavior.

PS-ThP13 Challenges in 0.1µm Line and Space Nitride Hard Mask Etching*, **Y.S. Chae**, J. Kim,* Samsung Semiconductor R&D Center, Korea*; W.M. Ahn, J.W. Shon,* Lam Research Corporation*; W.S. Lee, I.S. Kim, Y. Kang,* Samsung Semiconductor R&D Center, Korea*; J.P. Lee, B.K. Kong,* Lam Research Corporation*; C.J. Kang, J.T Moon,* Samsung Semiconductor R&D Center, Korea

As device feature size shrinks near 0.1 micron, PR (Photo Resist) erosion, microloading and striation are all much more serious due to 3D effect. And the thickness of nitride hard mask also becomes higher to prevent the electric short between gate and contact during SAC (Self Aligned Contact) process. These lead to require PR selectivity higher up to 4. Since the vertical metal-etch traditionally produces positive CD (Critical Dimension) bias, the nitride hard mask etching needs to produce negative CD bias. Therefore, we need to etch PR with high selectivity and negative CD bias, which is in trade-off relations. We have characterized the process trends in CD bias, striation and PR selectivity of nitride hard mask etching in terms of additive chemistry, RF power and its ratio. Best process results show narrow process window for relatively lower power with narrow range of O2 flow. Successful results for 0.09 micron process are obtained for lower ion energy process with high Ar flow.

PS-ThP14 Trench Etch Characteristics of Via-first Dual Damascene Process on 0.15µm SRAM Technology.*, **W.-S. Kim**,* Hynix Semiconductor Inc., South Korea, Korea*; J.-I. Cho, I.-S. Choi, J.-J. Lee, H.-S. Shin, H.-S. Yang,* Hynix Semiconductor Inc., South Korea

Recently, via-first dual damascene process with cost-effectiveness and fabrication complexity reduction has been proposed as an alternative to get over the limitation of conventional interconnection processes. However, it has some problems such as the formation of the fence and the facet around the via hole in the trench etching process. Especially, the fence can cause bad via hole filling and the incomplete removal of resist residues. In this study, we investigated the effect of CH2F2 and CO addition into C4F8 plasma on fence formation, and also relationship between organic ARC fill thickness and fence formation. Physical features were analyzed with SEM and TEM. And electrical characteristics were examined with continuity/bridge patterns. For the surface analysis, the etched oxide films with C4F8/CH2F2 and C4F8/CO, respectively, were characterized with XPS. In the trench etching with C4F8/CH2F2 plasma, the fence height was increased with organic ARC thickness. Since the organic ARC on the sidewall of the via hole played a role as the etch barrier during trench etching, fence-shaped oxide residue was occurred around the via hole. Moreover, in this study, we could also observe the fence profile in a condition of no organic ARC with C4F8/CH2F2 plasma because the polymer deposited at the top edge of the via hole prevented oxide etching around the via hole whereas fence free with C4F8/CO plasma. The XPS surface analysis data clearly showed that C4F8/CH2F2 plasma had higher intensity for C-C bonds and C-H bonds in comparison with C4F8/CO plasma. Therefore, in order to obtain fence-free trench profiles, optimization of ARC thickness and also use of low polymerizing plasma were simultaneously needed. Consequently, for 0.15µm SRAM technology, the fence-free trench etching was achieved with low polymerizing C4F8/CO plasma and optimum ARC fill thickness which was slightly lower than the etch stopper in the via hole.

PS-ThP15 Etching Characteristics for Porous Silica (k=1.5) by Using NLD Plasma in a Low Pressure*, **Y. Morikawa**, N. Mizutani, T. Hayashi,* ULVAC Japan Ltd., Japan*; T. Uchida,* ULVAC Japan Ltd.

The etched profile of the porous silica@footnote 1@ (produced in ULVAC Japan Ltd.) was obtained as an almost vertical structure. The etch rate was approximately 2 times higher than that of the SiO@sub 2@ film when linear saturated perfluoro carbon compounds were used,@footnote 2@ because the overall film density of the porous silica is low. However, in the case of C@sub 4@F@sub 8@ (Octafluorocyclobutane) plasma, the etch rate ratio to the SiO@sub 2@ was about 1.45. When C@sub 4@F@sub 6@ (CF@sub 2@=CFCF=CF@sub 2@: Hexafluorobutadiene) was used, the etch rate ratio was also very low (0.6). So the etch rate strongly depends on the gas structure, whereas the SiO@sub 2@ etch rate is almost constant. The Vpp of the RF bias was almost same for all kind of fluorocarbon gases. It was observed that CxFy@super +@ ions were main species in the C@sub 4@F@sub 8@ or C@sub 4@F@sub 6@ plasma (QMS) and a polymer film was formed on the etched surface (XPS). Therefore, it is considered that the fluorocarbon polymer formed in the pore suppresses the etch rate of the porous silica in the C@sub 4@F@sub 8@ or C@sub 4@F@sub 6@ plasmas. C@sub 3@F@sub 7@I (CF@sub 3@CFICF@sub 3@: 2-iodoheptafluoropropane) gas was examined. The etch rate selectivity of photo resist to porous silica went up about 50%, compared with C@sub 3@F@sub 8@. Negative F@super -@ ion in the C@sub 3@F@sub 7@I plasma was obtained as a very small peak, contrary in the C@sub 3@F@sub 8@ and other fluorocarbon plasmas. On the other hand, I@super -@ ion intensity was very strong. These results may imply that the iodine in the plasma plays some roles for etching. @FootnoteText@ @footnote 1@C. Tanaka and H. Murakami, Extended abstract (The 61st Autumn Meeting, 2000); The Japan Society of Applied Physics, 750 (4a-P4-27). @footnote 2@Y.Morikawa et al., J.Vac.Sci.Technol.A19(4), Jul/Aug (2001).

PS-ThP16 Trench Etch Challenges in a Cu/Low-k Via-First Dual Damascene Scheme*, **P. Jiang**, H. Hong, Q. Hong, K.J. Newton,* Texas Instruments, Inc.

In a via-first copper dual damascene integration scheme, trench patterning is one of the most critical steps, for both lithography and etch. Due to via topography, resist thinning occurs in dense via region during trench pattern, resulting in potential resist breakdown during trench etch. To prevent trench bridging or metal shorting, it becomes necessary to keep good trench etch profile and high resist selectivity. However, another key issue for trench etch is oxide ridge formation around vias which can disrupt metallic barrier and copper deposition resulting in degraded device reliability. In achieving good trench profile and high resist selectivity, oxide ridges often become severe. Therefore, it is very challenging to control profile, resist selectivity and oxide ridge formation simultaneously. In this paper, we will discuss the options and results that meet the special requirements for Cu/low-k dual damascene trench etch. The low-k dielectric film used in this work was an organosilicate glass (OSG). The effect of etch process parameters on trench profile, resist selectivity and ridge formation will be discussed, along with the resist effect on resist etch selectivity. Electrical results showing significant yield improvement with the optimal etch process will also be reported.

PS-ThP17 N@sub 2@ Addition Effect on Highly Accurate Organic Low-k Etching Process*, Y. Morikawa,* ULVAC JAPAN Ltd., Japan*; M. Ozawa, N. Mizutzni,* ULVAC JAPAN Ltd.*; **T. Hayashi**,* ULVAC JAPAN Ltd., Japan*; T. Uchida,* ULVAC JAPAN Ltd.

Etchings for organic low-k materials, FLARE@super TM@ and SiLK@super TM@, had been carried out at a N@sub 2@ dominant mixing ratio in an N@sub 2@ + H@sub 2@ plasma generated by the magnetic neutral loop discharge (NLD) method at low-pressure below 1 Pa.@footnote 1@. We had tried to control micro-trench free profile by using nitrogen-organic surface reactions in a fine pattern etch process. As the result, we were able to successfully control the profiles without micro-trench when the substrate temperature was kept above 0°C, blow 1 pa. Usually, when the N@sub 2@ + H@sub 2@ plasma with H@sub 2@ dominant mixing ratio or only NH@sub 3@ plasma is used, bowing profiles were obtained such a substrate temperature. However, the plasma with the N@sub 2@ dominant mixing ratio was used, bowing did not occur in the temperature range of 0°C to 30°C. Under this condition, the N1s/C1s ratio on the etched surface increased with increase of the temperature. This may be due to an enhancement of nitrogen addition reactions on the surface and thereby the sidewall is passivated. Negative ions in the H@sub 2@+N@sub 2@ plasma were measured by using a quadrupole mass spectrometer. NH@sub 2@@super -@ and CN@super -@ negative ions were observed as main peaks. These species decreased with the pressure. The CN@super -@ ion signal abruptly decreased at the end point. We will also report a finely deep etching process over 1.0 µm without any micro trench and without pillar residues on the etched surfaces. @FootnoteText@@footnote 1@Y. Morikawa et al, Proc.Symp.Dry Process, 263 (2000) @footnote 2@Y. Morikawa et al, J.Vac.Sci.Technol.,A19 (4), Jul/Aug (2000).

PS-ThP18 Damage Free Gate Shrinkage Method Using Low Temperature Si@sub 3@N@sub 4@ Film Deposition and SF@sub 6@/O@sub 2@ Gas Mixture Etching*, **C.R. LIM**, J.H Shin,* LG-Elite (LG-Electronics Institute of Technology), South Korea

Recently, the concern about sub micron gate length formation method for development of high performance FET is increasing. But, sub micron gate length could not be gotten using optical contact aligner or cheap stepper machine. And, in order to reduce resistance in FET gate electrode which had short gate length, we use normally T-shaped gate whose head was wide about 1 micrometer. In our lab, we tried to make FET whose gate length was shorter than the exposed gate length. After lithography of about 0.4 micrometer gate length using stepper, and we deposited silicon nitride film at low temperature to protect photo resist from deformation and at low work pressure to form conformal shape. Deposited silicon nitride film was etched using conventional RIE medium-pressure reactor and we tried to find proper etch condition from varied SF@sub 6@/O@sub 2@ gas ratio and could know proper etch condition of the ratio 3:7 at work pressure 100mTorr and RF power of 100watt. Doing so, we could get FET which has gate length of 0.1 micrometer and the deposition and etching condition harm no damage on wafer surface. In order to find low temperature silicon nitride film deposition condition and directional etching condition, we used SEM, optical emission spectroscopy and dielectric constant measurements.

PS-ThP19 A Study on the Polymer Residues Formation at the Via-hole and its Removal by Remote Oxygen/Nitrogen and Hydrogen Plasma*, **S.B. Kim**, H. Soh, Y. Kim, Y.C. Kim, H. Jeon,* Hanyang University, Korea

For multilevel device fabrication, via-holes are generally dry etched for electrical connection between the upper and lower metal layers.@footnote 1@ The ashing and photo resist (PR) strip processes are generally followed to remove the PR and polymerized residues, respectively.@footnote 2@ However, the PR strip is the wet chemical process and causes environmental problems. In this study, low temperature remote plasma dry cleaning process that removes both the PR and polymer residues containing carbon and fluorine will be described. The radio frequency remote oxygen/nitrogen plasma was used to remove the PR and polymer residues simultaneously. The cleaning efficiency was systematically evaluated at various conditions such as the oxygen and nitrogen ratio, plasma power, exposure time, gas flow rate and sample temperature. The hydrogen plasma treatment was also carried out to remove polymerized residues formed at the bottom nitride layer oxygen/nitrogen plasma cleaning. In-situ Auger electron microscopy, X-ray photoelectron spectroscopy, atomic force microscope analysis systems were used to evaluate the cleaning effects and to avoid recontamination such as carbon absorption in the air. Scanning electron microscope provided a preliminary assessment of cleaning performance. Preliminary results indicated that the hydrogen plasma treatment subsequent to oxygen/nitrogen PR ashing process was very efficient to remove the polymerized residues formed at the bottom nitride. @FootnoteText@ @footnote 1@D. Louis, E. Lajoinie, W. Mun Lee, D. Holmes, Microelectronic Engineering, 41/42, 377-382 (1998) @footnote 2@Ying Wang, Sandra W. Graham, Lap Chan, SheauTan Loong, Journal of Electrochemical Society, 144, 1522-1528 (1997)

PS-ThP20 Studies on Photoresist Etching in Inductively Coupled Plasmas*, **X. Xu**, P. Shoenborn,* LSI Logic

Bottom anti-reflective coatings (BARCs) are now used in applications such as gate patterning that requires the tight critical dimension (CD) control. BARC removal must be accomplished before the film (e.g. poly and dielectric) is etched. BARC etch is a critical step that can affect the final line width of the etched features. In general, an oxygen plasma with additives is used to etch BARC, in which photoresist has been trimmed simultaneously. In this work, the effect of O@sub 2@/N@sub 2@ and O@sub 2@/He plasmas on etching of photoresist is investigated on Lam TCP 9400PTX system. The self-bias voltage on the wafer has been measured for a variety of conditions with different top source powers, bottom bias powers, gas mixtures and gas flow rates. The results show that compared to O@sub 2@/N@sub 2@ plasma, the self-bias voltage is lower and the etching rate of resist is higher for O@sub 2@/He. Our measurements indicate that the etched products can lead to an increase of self-bias voltage with a fixed bias power. The influence of etched products is due to the decrease of the ion flux to wafers, which is shown through the use of plasma simulator, the Hybrid Plasma Equipment Model (HPEM).

PS-ThP21 Method to Prevent Notching in Polysilicon Gate Etch Process with Long Over-Etch*, **W. Pau**, M. Shen,* Applied Materials

In this study, we investigate the factors that can prevent notching in polysilicon gate etch process with very long over-etch. Conventionally, process optimization focuses on varying the parameters in over-etch to prevent notching. The effect of main etch and the interactions of main etch and over-etch are often overlooked. This paper explores the effect of main etch as well as the coupling between main etch and over-etch in notching elimination. The process consists of a timed main etch 1 (ME1) with CF@sub4@/Cl@sub2@/N@sub2@ chemistry followed by a HBr/Cl@sub2@/He-O@sub2@ main etch 2 (ME2) step . Then a high selectivity over-etch (OE) step uses HBr/He-O@sub2@ to etch any remaining polysilicon residue. ME2 matrix results reveal that this step plays a significant role in notching prevention. For ME2 step, a high pressure, high bias power, high HBr/Cl@sub2@ ratio and high He-O@sub2@ flow are most effective in preventing notching. For OE step, low pressure, low He-O@sub2@ flow and low source power are most effective in prevent notching. There are two main mechanisms that are responsible for notching prevention in ME2: (1) profile modification through ME2 and OE interaction and (2) sidewall passivation enhancement by ME2 only. High pressure in ME2 prevents notching through the first mechanism by having a taper profile after ME2 endpoint. This profile is then modified by OE so that a vertical profile is achieved. The effect of bias power in notching reduction, on the other hand, is attributed to the second mechanism. High bias power densifies the sidewall passivation to provide better protection at the bottom of the film, thus preventing notching.

PS-ThP23 Chemical Mechanisms of the Etching and Non-etching of Magnetic Materials in CO/NH@sub 3@ Plasmas*, A.S. Orland,* Auburn University*;* ***R. Blumenthal,*** Auburn University, usa

The etching of Fe, Ni and Co foils in CO/NH@sub 3@ plasmas have been investigated using supersonic pulse plasma sampling mass spectrometry. It has been previously reported@footnote 1@ that plasmas based on high mole fractions of CO are observed to result in the deposition of carbide films, while pure NH@sub 3@ plasmas and high NH@sub 3@ content mixtures are reported to etch the metals, with a maximum etch rate of 500A/min at ~ 13% CO in NH@sub 3@. Mass spectra were collected over the entire range of composition from 100% CO to 100% NH@sub 3@ plasmas. In pure CO plasmas, the major plasma products that were observed are CO@sub 2@, C@sub 2@O@sub 2@, C@sub 2@O@sub 3@ and C@sub 3@O@sub 2@. The addition of NH@sub 3@ to the feed gas results in a complete elimination of the C@sub 3@O@sub 2@ species at ~60% CO, while C@sub 2@O@sub 3@ persists to ~40% CO. As the C@sub 3@O@sub 2@ and C@sub 2@O@sub 3@ disappear, a series of peaks around N@sub 4@H@sub 6@ appears. The CO@sub 2@ signal initially decreases rapidly as the CO composition is lowered to ~60%, and then remains relatively constant until disappearing completely in the 100% NH@sub 3@ plasma. The C@sub 2@O@sub 2@ species, believed to be a weakly bound dimer, is the only product that shows a smooth transition to nitrogen containing analogs as the NH@sub 3@ percentage increases. C@sub 3@O@sub 2@ is well-know to act as a carbon atom donor, through successive losses of CO, and consequently, it is concluded that this species is responsible for the deposition of the carbide layer that inhibits the etching of metals in pure CO plasmas. The rapid suppression of the chemical sequence responsible for forming this species, as NH@sub 3@ is added, makes etching possible for higher fractions of NH@sub 3@ in the plasma. @FootnoteText@ @footnote 1@ K.B. Jung, et al. J. Vac. Sci. Technol. A 17(2), 535 (1999)

PS-ThP24 Resist Trimming Process Using High Density Plasma for Sub-0.1µm MOSFET*,* ***C.Y. Sin,*** *B.H. Chen,* National University of Singapore*; K. Loh, P. Yelehanka,* Chartered Semiconductor Manufacturing, Singapore

Because of the resolution limit of the 248nm lithography and immaturity of the 193nm lithography process, resist trimming process using oxygen containing gas mixture has been developed for sub-0.1@micro@m MOSFET fabrication. In this paper, the characteristics of resists trimming in high-density plasma were investigated. Experimental results are presented to show the trimming behavior of resist as a function of RF source power, bias power, temperature, linewidth to space ratio, gas composition and reactor pressure. Effect of gas composition on trimming process were evaluated using three different gas mixtures: HBr/O@sub 2@ and Cl@sub 2@/O@sub 2@ as well as CF@sub 4@/O@sub 2@. The gas mixture of CF@sub 4@/O@sub 2@ gives high trim, improved resist sidewall roughness and good uniformity. Studies of X-ray photoelectron spectroscopy (XPS) will be performed to determine the chemical composition of the resist sidewall passivation. The features studied comprised of alternate polysilicon lines and spaces. The amount trimmed is linearly proportional to trim time. For resist trimming, the experimental results revealed that the trimming process is of very feature density dependence. rim rate is dependent on linewidth to space ratio, but is independent of initial linewidth for the same linewidth to space ratio. Trim rate increases at low CF@sub 4@ gas flow ratio and then decreases. Trim rate of 0.66@micro@m/min can be achieved. The activation energies of trimming for dense and isolated line are found to be 0.13eV and 0.128eV, respectively, at gas composition of 100sccm CF@sub 4@/30sccm O@sub 2@ but have quite different pre-exponential constants, which suggests to be feature density dependence. Bias power has no significant effect on trim rate. Reactor pressure in the range from 5mTorr to 20mTorr also does not affect much the trim rate. The resist trimming process is found to be reproducible and controllable, making it a useful process for nanometer-scale device fabrication.

PS-ThP25 The Geometric and Chemical Effect of Polymer Deposition and Etch-product Redeposition on the Etching of SiO@sub 2@ Trench Sidewall in a CF@sub 4@ Plasma*,* ***J.H. Min,*** *S.W. Hwang, G.R. Lee, S.H. Moon,* Seoul National University, Korea

The effect of etch-product redeposition on the etching of SiO@sub 2@ trench sidewall in a CF@sub 4@ plasma was studied using a Faraday cage with a slit on the upper plane located in a transformer coupled plasma reactor. The Faraday cage with a slit allowed ions to be injected vertically on the specified portion of SiO@sub 2@ bottom surface under the practical plasma condition. The effect of the bottom surface on the redeposition of the etch products on the sidewall was studied by comparing the properties of the sidewall surfaces obtained with or without the etch-product emission from the bottom surface. The trench bottom was etched at the bias voltage ranging between -200 and -600V and at the source power between 200 and 600W. The bias voltage and the source power had complex influences on the redeposition of the etch products on the sidewall because they changed the concentration of radicals, and the flux and the energy of ions injected on the bottom surface. Specifically, the bias voltage increased the redeposition rate mostly by physical sputtering, while the source power increased the rate mostly by chemical sputtering. The concentration of CF@sub 2@ and F radicals increased with the bias voltage and the source power, which enhanced the polymer deposition on the sidewall. The shape of the Si-O peak in the Infrared(IR) spectrum of the redeposition film was similar to that of thermal oxide, but the Auger Emission Spectroscopy(AES) indicated that the O/Si ratio was higher for the redepsition film than for the thermal oxide. Analyses of the sidewall surface by AES and IR indicated that F radicals reacted with the oxide layer to break the Si-O bond. In the case of oxygen addition, the etch rate of the bottom surface increased but the rates of redeposition and polymer deposition on the sidewall decreased due to the enhanced production of F radicals in the plasma.

PS-ThP26 Evaluation of High Temperature Process in W/poly Si Gate Stack Etching in a Dual Frequency Plasma Reactor*,* ***J. Hong,*** Samsung Electronics, Korea, South Korea*; J.S. Jeon, C.J. Kang,* Samsung Electronics, Korea

W/poly Si stack becomes potential candidate in giga bit DRAM gate structure due to its lower sheet resistance compared to WSi/poly Si stack. Emerging process issues in W gate module are high etch selectivity of W over Si@sub 3@N@sub 4@ mask and poly Si stack down for self aligned contact scheme. High temperature process was evaluated in W etching to achieve high etch selectivity based on Cl@sub 2@/O@sub 2@ gas chemistry in a dual frequency plasma reactor. Mask loss and W profile were found to be strong function of gas ratio, process pressure and ion energy. The presence of oxygen inhibited Si@sub 3@N@sub 4@ mask loss by oxidation while enhancing W etching at high process temperature (150°C). Two steps W etch was developed in order to reduce the recess of poly Si in W overetch step. Poly Si recess showed a different behavior with Cl@sub 2@/O@sub 2@/NF@sub 3@ based gas chemistry at the temperature raging from 100°C to 150°C. Recess was optimized at 120°C at the expense of mask loss and W profile. Conventional HBr based chemistry appeared to have inability to provide sidewall passivation in poly Si etching at high temperature. Gas chemistry for sidewall passivation and high selectivity over gate oxide at high temperature will be discussed.

PS-ThP27 The Effect of Reflected Ions on the Etching of Silicon Dioxide Surface in the Fluorocarbon Plasma*,* ***G.R. Lee,*** *S.H. Hwang, J.H. Min, S.H. Moon,* Seoul National University, Korea

In the plasma etching process, ions reflected from the sidewall surface of a deep, narrow pattern contribute to the additional etching of the other surfaces, which may be called as a secondary etching. When the aspect ratio of the etched pattern becomes high, the influence of the secondary etching on the etch profile becomes significant. In spite of its importance, however, the secondary etching due to the reflected ions has not been studied much especially under the conditions of industrial plasma processes. In many cases of the etch-profile simulation, it has been commonly assumed that ions reflect from the sidewall in an elastic-specular mode, particularly when the ion-incident angle is high. In this study, we observed the position and the extent of the secondary etching of silicon dioxide in a fluorocarbon plasma due to the reflected ions with various incident angles. The ion angles were controlled by using a Faraday cage and specially fabricated sample holders placed in a plasma reactor. The experimental results deviated from those predicted based on an elastic-specular assumption when the ion-incident angles were close to 90°. According to the analysis of the substrate surface after the plasma etching, the deviation of the ion reflection from the elastic-specular mode originated from the deposition of a fluorocarbon film on the substrate surface. The film-deposited surface became rough, and consequently ions reflected from the surface in a non-elastic, non-specular mode.

PS-ThP28 Effect of Ion Bombardment on Developed Photoresist Morphology during Reactive Etch Processes for sub 0.25 micron Semiconductor Devices*,* ***M. Naeem,*** *R. Wise,* IBM Microelectronics Division*; F. Wang,* Cypress Semiconductors*; G. Worth, D. Dobuzinsky,* IBM Microelectronics Division*; Z. Lu,* Infineon Technologies*; A. Hadi,* Conexant

The use of advanced resist systems has become necessary for lithography in processing of advanced (sub 0.25 Âµm) semiconductor devices to achieve acceptable image quality. These novel resist systems are more sensitive to both post exposure treatments as well as the ion bombardment component present in reactive ion etch (RIE) processes. We discuss the impact of resist interactions with low energy plasma and morphological changes in the resist profile. In particular, the effects of different photoresist constituents, post develop bake conditions, various RIE steps and RIE parameters in capacitively coupled plasma (CCP), magnetically enhanced RIE (MERIE) and inductively coupled plasma (ICP) systems on resist morphology and the quality of final etched images are presented.

PS-ThP29 Study on the Low Angle Forward Reflected Neutral Beam Etching System*, **D.H. Lee**,* Sungkyunkwan University, Korea*; J.W. Bae,* Sungkyunkwan University, Korea, South Korea*; S.D. Park, G.Y. Yeom,* Sungkyunkwan University, Korea

Plasma etching is one of the key technologies in the fabrication of deep submicron silicon based integrated circuit. However, plasma etching could give serious disadvantages due to the energetic charged particles generated in the plasma which cause radiation damage such as physical defect, increased gate oxide breakdown, charging, etc. To avoid these charge-related and physical impact-related damages, several low-damage processes have been proposed. One possible alternative to avoid these problems is a low energy neutral beam etching. In this study, neutral beam has been generated using a low angle forward reflected neutral beam and its characteristics such as the degree of neutralization, etch characteristics, etc. have been studied as a possible anisotropic etching technique without charging. When the reactive ion beam was reflected on a reflector at the angles lower than 15°, most of the ions reflected were neutralized and also the lower reflector angle showed the higher degree of neutralization. Complete removal of the ions in the reflected beam could be accomplished by installing a retarding grid system between the sample and the reflector and by applying a potential higher than the maximum ion energy of the flux. This reflected neutral beam source has been devised to be scaleable to a large diameter and also to etch polymer and SiO@sub 2@ anisotropically. In order to obtain a large flux from the ion source, inductively coupled plasma was used as the plasma source and specially prepared extraction grids which have very dense and small holes were used. Details of the developed neutral beam source and its properties will be discussed in addition to the etch characteristics obtained using the low angle reflected neutral beam source.

PS-ThP30 Highly Selective Etching of Al/AlN Structures for Metallization of SAW Devices*, **F. Engelmark**, I.V. Katardjiev, G.F. Iriarte,* Uppsala University, Sweden

Metallization is a critical step in the fabrication of high frequency thin AlN film based SAW devices. Both state-of-the-art lithography as well as high selectivity and anisotropy during etching of Al with respect to AlN are required for low loss and high performance devices. In this work, the etch rates of reactively sputtered AlN, sputtered Al, thermal SiO@sub 2@ and Shipley 1813 photo resist as well as the selectivity between Al/AlN, Al/SiO@sub 2@ and resist/Al have been systematically studied during ICP RIE. Emphasis is focused on obtaining high Al etch rates, while at the same time keeping the etch rate of AlN and that of the resist sufficiently low. High anisotropy is obtained by passivating the sidewalls by the addition of oxygen. The recipe developed is based on a modified Al etch using a mixture of BCl@sub 3@, Cl@sub 2@, O@sub 2@ and Ar. The parameters varied were gas composition, process pressure, substrate bias and ICP power. Generally it is found that the Al etch rate exhibits a maximum with the O@sub 2@ flow, while the AlN etch rate decreases monotonically. Substrate bias is found also to be an important parameter with respect to both etch rates and selectivity. At optimized conditions (500 W ICP power, 35 W chuck power, 50 sccm BCl@sub 3@, 25 sccm Cl@sub 2@, 10 sccm O@sub 2@, 0 sccm Ar, pressure 10 mTorr) the Al etch rate is 1700 nm/min with a selectivity of 58 towards AlN and 10 towards the resist. The same recipe, slightly modified, has also shown similar Al etch rates when etching Al over SiO@sub 2@ with a selectivity of up to 180. High anisotropy of the Al etch rate is observed with increasing O@sub 2@ flow. The former has been determined from cross-sectional SEM observations.

PS-ThP31 W/WNx/Dual-Poly Stack Gate Etching for 0.15 µm Tech. Full CMOS SRAM*, **B.-K. Lee**, Y.-J. Choi, I.-K. Yang, I.-S. Seo, H.-S. Shin, H.-S. Yang,* Hynix Semiconductor Inc., South Korea

As SRAM cell composed of pMOS and nMOS is scaled down to deep submicron regime, the surface channel pMOS with p+ poly Si gate is a key technology to realize high performance full CMOS SRAM device, because of its strong immunity to short channel effect. Another important issue to be considered with scaling down of the device is reduction of resistance-capacitance delay along channel width. The W/WNx/Dual-Poly stacked-gate electrode is promising method for these requirements. In the present study, we investigated the effect of gas chemistry on the W/WNx etching characteristics such as profile angle, surface morphology of poly Si and selectivity of the W/WNx over SiON hard mask and poly Si, respectively. Physical features were analyzed with SEM and TEM, and electrical properties were measured. The surface analysis of etched W/WNx film with XPS and plasma analysis with L/P(Langmuir Probe), OES(Optical Emission Spectroscopy), RGA(Residual Gas Analysis), and Posi-SIMS were also performed. When Cl2 was added to NF3, the laternal etching in W/WNx was suppressed due to increase of polymerization. In addition, the selectivity of the W/WNx over SiON was improved by the increase in etch rate of W/WNx and also the decrease in that of SiON induced from the change of plasma state. In case of Ar and O2 addition, the selectivity of W/WNx over poly Si was increased, and consequently sublayer poly Si loss was reduced during over etching. Finally, the addition of CF4 to NF3 made the surface morphology of poly Si smooth resulting from more uniform W/WNx etching during the over etching. On the basis of these results, W/WNx/Dual Poly stack gate etch process having a vertical profile, no sub Si attack and no residue could be achieved with NF3/Cl2/CF4/O2 gas for W/WNx etch and with HBr/Cl2/O2 gas for poly Si etch for 0.15 Tech. SRAM and beyond. Keywords: etching, tungsten, dual gate, SRAM, surface channel pMOS.

PS-ThP32 Trimming Photoresist in a DPS(TM)II 300mm Poly Etch System - Control of Trimming Rate, Uniformity and Stability*, **M. Shen**, O. Yauw, N. Gani, C. Lin, Y. Lai, M. Chu,* Applied Materials

As the IC industry aggressively moving towards 0.10um gate length devices, requirements on CD control become increasingly difficulty to meet. Resolving 0.10um line width with great accuracy and uniformity on 300mm wafer is a major challenger for conventional photolithography technology. Therefore, trimming photoresist through etching has become a very attractive alternative to speed up the road map towards 0.10um technology using existing photolithography. Resist trimming, however, requires strict control of trimming rate, uniformity and stability. Trimming linearity is another important element for precise CD control. With integrated CD metrology approach, it is possible to adjust the trimming time based on in-coming wafer to obtain desired final CD for each wafer. The study presented here outlines some of the development works for resist trimming process on Applied Materials DSP(TM)II 300mm poly etcher system. Trimming up to 30nm with less than 5nm in range uniformity has been achieved on 300mm wafers. Excellent CD uniformity controls on overall process involving trimming, hardmask and polysilicon gate were demonstrated on DPS(TM)II 300 system.

PS-ThP33 Effects of Gas Chemistry of Inductively Coupled Plasmas on the Multi-Layer Gate Metal Etching Characteristics for TFT-LCD Devices*, **Y.J. Lee**,* Sungkyunkwan University, Korea, South Korea*; C.H. Yi, B.K. Song, M.J. Chung,* Sungkyunkwan University, Korea*; M.P. Hong,* Samsung Semiconductors, Korea*; G.Y. Yeom,* Sungkyunkwan University, Korea

For advanced TFT-LCD manufacturing processes more conductive gate materials are required for the next generation large size and the high quality of thin film transistor liquid crystal displays (TFT-LCDs). For gate metal layer, single gate metals such as Al-Nd and Ag, and double gate metals such as Al-(Cr, Mo, MoW, or W) are widely studied. Currently, the patterning of gate metals is done by wet etching methods. With the wet etching method, however, the tapered patterning of Al-alloy mentioned above is nearly impossible. Also, most of the capacitively coupled RIE-type equipments available for FPD devices are suffered from relatively low plasma densities, therefore, low etch rates. Therefore, in this study, the tapered etching of multi-layer gate metals such as Ag, Al-Nd, and double gate metal films (Al-Cr, Mo, W, or MoW) deposited on glass substrates were studied using high density inductively coupled plasmas (ICP) and the etch characteristics were investigated as a function of gas combination, pressure, dc self-bias voltage, and inductive power. Chlorine and bromine-based gas were used with N@SUB 2@, O@SUB 2@, and Ar as additive functional gases. Depending on the materials, the different etch rates were obtained for the same process parameter condition. For example, the etch rates close to 1500Å/min could be obtained using BCl@SUB 3@/HBr chemistry for Al-Nd etching and the etch selectivity over photoresist was close to 1. The low etch rates were attributed to the Nd in Al. Using the plasma diagnostic tools such as optical emission spectroscopy and quadruple mass spectroscopy, the etching mechanisms of various gate metal layers with these chemistries were investigated. Variations of surface composition for various gas mixtures were also investigated using X-ray photoelectron spectroscopy. The etch profiles and surface defects were observed with a scanning electron microscope.

PS-ThP34 The Influence of Ar Flow Rate on Photoresist Selectivity in High Density Plasma Etching of SiO@sub2@*, E. Haikata,* *S. Sasaki, T. Yoshida, K. Nojiri,* Lam Research Co., Ltd, Japan

As dimension of LSI becomes smaller, higher photoresist selectivity to SiO@sub2@ is required in high-aspect-ratio contact hole etching, because photoresist mask becomes thinner to get enough resolution. Although C@sub4@F@sub8@/Ar/O@sub2@ gas chemistry is widely used for SiO@sub2@ etching, the influence of Ar flow rate on photoresist selectivity is not clear. This paper presents the influence of Ar flow rate on photoresist selectivity and etching profile along with the discussion on the basis of XPS and OES analysis. In the experiment, Ar flow rate was changed from 50 sccm to 500 sccm in Transformer Coupled Plasma Etcher, with C@sub4@F@sub8@/O@sub2@ flow rate kept constant. With increasing Ar flow rate, photoresist selectivity increased because the photoresist etch rate decreased drastically, while the SiO@sub2@ etch rate decreased only slightly. In contrast, at low Ar flow rate, photoresist selectivity dropped remarkably at small diameter holes due to RIE Lag, and etch stop was observed. XPS data showed that polymer deposited on the photoresist at high Ar flow rate contained more C-C and C-CF@subx@ chain, and it was more C rich. From OES results, C@sub2@/CF@sub2@ ratio increased as Ar flow rate increased. Since C radical has higher sticking coefficient than CF@sub2@ radical, C is thought to deposit at the upper part of the contact hole and photoresist surface, leading to higher selectivity because C rich polymer has high resistance to plasma attack.On the other hand, CF@sub2@ is thought to go into inside of the hole, causing etch stop at low Ar flow rate. We conclude that high Ar flow rate has advantage of wider etch stop margin and higher photoresist selectivity.

PS-ThP35 Novel Organic Low-k Dielectric Etching by Using CH@sub 3@NH@sub 2@ / N@sub 2@ Plasma*, H. Nakagawa,* Matsushita Electric Co., Ltd., Japan*; Y. Morikawa, T. Hayashi,* ULVAC JAPAN Ltd., Japan

A Novel organic low-k etching has been developed by using a new gas chemistry of CH@sub 3@NH@sub 2@ / N@sub 2@ in a neutral loop discharge (NLD) plasma system. The organic low-k etching produces normal taper profile, no micro-trench, and small hard-mask erosion, which required for fabricating Cu / organic low-k damascene multilevel interconnects. The concept of etching is to introduce C-H passivation film with appropriate thickness on sidewall and bottom of etched patterns, and employing CH@sub 3@NH@sub 2@ / N@sub 2@ has led to the achievement of the required performance. Furthermore, we can control the taper angle of the etched profile by changing a flow ratio of CH@sub 3@NH@sub 2@ / N@sub 2@ and N@sub 2@ in this chemistry. We have already reported that the via hole etching with normal taper profile, no micro-trench and small hard-mask erosion is obtained by using a gas mixture of CH@sub 4@ / N@sub 2@ in neutral loop discharge (NLD) plasma.@Footnote 1@ In this chemistry, we were able to obtain only slight taper angle and small etch rate of photo-resist (PR) mask. The organic low-k etching by CH@sub 3@NH@sub 2@ / N@sub 2@ plasma, however, has also overcome the problems which were not achievable in the etching by CH@sub 4@ / N@sub 2@ plasma. In this presentation, we will discuss the concept of etching gas chemistry design and the etching mechanism on the basis of both QMS measurement results of plasma gas phase and composition evaluation results of the deposition film formed on the Si wafer surface during etching. @FootnoteText@@footnote 1@ H. Nakagawa et al, Tech. Dig. of Dry Process Symposium, Tokyo, 257 (2000).

PS-ThP36 Low Temperature Etch Characteristics Using 193 nm ArF Photoresist Below 0.1µm Device*, W.S. Lee,* Samsung Electronics, South Korea*; J.W. Shon, B.K. Kong,* Lam Research Corporation*; J. Kim,* Samsung Electronics, South Korea, Korea*; E.S. Chae,* Samsung Electronics, South Korea

Patterning sub 0.1 micron devices require a photoresist (PR) that is extremely photosensitive to short wavelength such as 193 nm ArF PR. However, etch problems associated with ArF PR includes higher etch rate, less selectivity, less PR thickness due to increasing opacity at shorter wavelength. For a nitride hard mask etching, process results are sensitive to process temperature. SEM pictures obtained from hard mask open process show notable improvements at -20Â°C. Wafer temperature measurements suggest that bulk wafer temperature is only about 10Â°C higher that chiller temperature. However, surface of PR could heat up to much higher than that of bulk wafer temperature, which could cause PR deformation.

PS-ThP37 0.1µm Line and Space Nitride Hard Mask Open Process Using Ar/C@sub 2@F@sub 6@/O@sub 2@ Plasma*, W.S. Lee,* Samsung Electronics*; **J.W. Shon**, B.K. Kong, E.A. Hudson,* Lam Research Corporation

Traditional line and space nitride hard mask open process uses Ar/CF4/CHF3/O2 recipes. The process chemistry using both CF4 and CHF3 combination provides excellent CD control with controllable amount of polymer needed for 0.14 micron and larger devices. However, as the feature size shrinks to 0.1 micron, better PR selectivity and CD control are required. Using C2F6 based recipe, we can double PR selectivity with minimum penalty in CD blow out. We have developed C2F6 based nitride hard mask open recipe in comparison to the baseline CF4 recipe. PR selectivity and profile are much better compared to CF4 based recipes. We are reporting process trends for C2F6 based line and space nitride hard mask open process with respect to total power, power ratio, effects of adding polymerizing gas, and striation issues.

Surface Science
Room 134/135 - Session SS1-ThP
Catalysis on Model Systems Poster Session

SS1-ThP1 A Model Catalyst in Motion: Restructuring of a Pt(110) Surface at Atmospheric Pressure*, **B.L.M. Hendriksen**, J.W.M. Frenken,* Leiden University, The Netherlands

The surface structure of a catalyst can depend on the reaction conditions. However, most model studies have been performed at well-defined, but strongly non-realistic, conditions such as ultrahigh vacuum or very low pressures. We have used a novel high pressure, high temperature scanning tunneling microscope, which is set up as a micro-flow reactor, to study a platinum (110) surface at semi-realistic conditions for CO oxidation, i.e. high pressure and temperature. Already a low partial pressures of CO induces the lifting of the Pt(110)-(1x2) missing row reconstruction [T. Gritsch et al., Phys. Rev. Lett. 63, 1086 (1989)] to form a tiger-skin like structure consisting of (1x1) patches. As soon we apply an atmospheric pressure of CO at 425 K, this intermediate structure coarsens to form smooth (1x1) terraces, as we have observed in STM-movies.

SS1-ThP3 Lateral Interactions in Elementary Surface Reactions between CO and NO on Rhodium Surfaces*, M.J.P. Hopstaken, A.P. van Bavel,* Eindhoven University of Technology, The Netherlands*; **J.W. Niemantsverdriet**,* Eindhoven University of Technology, The Netherlands, Netherlands

Unraveling catalytic mechanisms in terms of elementary reactions and determining the kinetic parameters of such steps is at the heart of understanding catalytic reactions at the molecular level. Here we report the use of temperature programmed desorption and static secondary ion mass spectrometry to study reactions between NO and CO on Rh(100) and (111). On both surfaces the reaction rates of the different elementary steps depend highly on coverage. At low coverage, dissociation of NO is completed around 250 K and 340 K for the Rh(100) and the Rh(111) surface, respectively. When the surface is saturated with NO, dissociation only starts when some NO desorbs first, i.e. when empty sites become available. However, inhibition of NO dissociation at intermediate coverages cannot be explained by site blocking alone, but is due to lateral interactions with other adsorbates such as N, O, and NO. Studying the effect of coadsorption of these species enables an estimate of the magnitude of these lateral interactions. The combined influence of lateral interactions and site blocking leads to explosive behavior in the CO + NO reaction on saturated surfaces. The explosion is triggered by the desorption of a small amount of CO. The liberated sites enable the dissociation of NO and the subsequent reaction of O-atoms with CO creates even more free sites. The process is autocatalytic in the free sites and becomes explosive. These explosions have been observed in real time with TPD and SIMS.

SS1-ThP4 Molecular Beam Study of the N@sub 2@O + CO Reaction on Rh(111)*, **S. Wehner**, F. Zaera,* University of California, Riverside

Rhodium is well known for its unique ability to reduce NO to N@sub 2@. It is this property that makes it indispensable in the three way catalysts used in cars to clean their exhausts. Former studies in this laboratory using molecular beams have shown that the catalytic reduction of NO by CO takes place at the periphery of surface islands of adsorbed nitrogen atoms, and most likely involves the formation a N-NO intermediate. Here, results from a kinetic study on the conversion of N@sub 2@O + CO mixtures on Rh(111) surfaces are presented. It was found that the overall behaviour is similar to that of the NO + CO reaction. The reaction rate with both nitrogen oxides reaches a maximum near 500 K for stoichiometric beams, but in the case of N@sub 2@O the rate-limiting step is the formation of CO@sub 2@, not the production of N@sub 2@ as when NO is used. These results will be contrasted with our previous work on the NO + CO and CO + O@sub 2@ systems to get an overall picture of the elementary steps involved in the cleaning of car exhausts.

SS1-ThP5 Oxygen Defect Structures and Diffusion of Surface Oxygen Atoms on CeO@sub 2@(111) Surface Studied by Noncontact Atomic Force Microscopy*, **Y. Namai**, K. Fukui, Y. Iwasawa,* The University of Tokyo, Japan

CeO@sub 2@ is widely used as a component of automobile catalysts, where CeO@sub x@ (x@<=@2) is believed to work as a buffer of active oxygen of the catalysts to the most efficient region for oxidation of CO and hydrocarbons in exhaust gas. Migration of surface oxygen atoms to active sites for the oxidation and surface structural changes in the reduction-oxidation cycles are crucial issues to understand the role of CeO@sub x@ in an atomic scale. Noncontact Atomic Force Microscopy (NC-AFM) is a recently developed technique to visualize surface structures in an atomic scale. We have applied NC-AFM to a CeO@sub 2@(111) surface and succeeded in obtaining atom-resolved images for the first time. By annealing an Ar ion-sputtered CeO@sub 2@(111) surface at 1173 K for 1 min, hexagonally arranged oxygen atoms with a constant separation of 0.38 nm were observed by NC-AFM. Oxygen point vacancies were found on the surface as dark depressions. Further annealing of the surface at 1173 K in vacuum increased the density of point vacancies and multiple defects began to appear from total annealing period of 4 min. Triangular defects which consist of neighboring three oxygen vacancies and line defects which consist of 2-4 oxygen vacancies along the [10-1] direction, the [0-11] direction, and the [1-10] direction were visualized by NC-AFM. Successive NC-AFM observation revealed that oxygen atoms on slightly reduced CeO@sub 2@(111) surfaces are mobile even at room temperature. Mobility of the surface oxygen atoms seems to depend on the density of surface oxygen defects. Such mobile oxygen atoms may be a key species in the oxidation reactions.

SS1-ThP7 Adsorption Geometry of Modifiers in Chiral Catalysis*, J. Kubota, **F. Zaera**,* University of California, Riverside

It has been recently determined that heterogeneous hydrogenation catalysts such as platinum can be made enantioselective by the use of molecular modifiers. For instance, alpha-ketoesters such as ethyl pyruvate can be selectively hydrogenated by cinchona-modified platinum catalysts to produce the corresponding optically-pure (R)- or (S)-alpha-hydroxoesters (ethyl lactates from the pyruvate). In these, the adsorption geometry of the modifier appears to be critical to the performance of the catalyst. Here we report on infrared studies on the characterization of the adsorption of those modifiers from the liquid phase onto platinum surfaces. A number of cinchona molecules were probed, and the effects of concentration and solvent on the adsorption were investigated.

SS1-ThP8 Combustion of Hydrogen Over a Palladium Catalyst Studied with Laser Induced Fluorescence Imaging*, **A. Johansson**, M. Forsth, A. Rosen,* Goteborg University and Chalmers University of Technology, Sweden

Catalysis is of great fundamental, practical and economical interest in today's society. Noble metals, such as palladium, is widely used as heterogeneous catalysts for reduction of emissions of car exhausts. It is therefore important to study the catalytic property of this metal. Combustion of hydrogen with oxygen was chosen as a model system to make it as simple as possible, avoiding hydrocarbons. The oxygen and hydrogen molecules adsorb and react via reaction intermediates to form water. An important intermediate is the OH molecule. The hydroxyl radical OH also has spectroscopic properties which make it convenient to study. Laser Induced Fluorescence (LIF) was used to investigate the gas-phase concentration of the OH molecule. An ICCD camera was used as detector to study the OH concentration profile in two dimensions outside the palladium surface. The polycrystalline palladium foil was resistively heated up to 1300K and nearby temperatures. The chamber was evacuated with roots and turbo pumps. The hydrogen and oxygen gas flow was regulated with two mass flow controllers, one for each gas. The mass flow controllers were calibrated with a quadropole mass spectrometer connected to the chamber. The working pressure in the chamber was varied from 0.1-100 Torr. The hydrogen/oxygen reaction on a hot palladium surface was also modelled using the Chemkin software package. Estimations of important reaction parameters could be achieved by comparing experimentally obtained OH-profiles with modelled profiles. Also, sensitivity analysis of the obtained model indicated which reactions that are rate-limiting and which reactions that are less important from a catalytic point-of-view. These last results should be taken as advises as to where future experimental efforts should be made. The water production rate is measured with micro calorimetry.

SS1-ThP9 Scanning Tunneling Microscopy Studies of the Growth and Morphology of Cu Clusters Deposited on TiO@sub 2@(110)*, **J. Zhou**, J.E. Reddic, D.A. Chen,* University of South Carolina

The growth of metals on oxide surfaces has become an important area due to the variety of applications involving metal-oxide interfaces. We have conducted scanning tunneling microscopy (STM) studies of Cu clusters grown on single-crystal TiO@sub 2@(110) (rutile) surfaces under ultrahigh vacuum conditions as a model for understanding the early stages of metal-on-oxide growth. Previous investigations of Cu deposited on TiO@sub 2@(110)-(1x1) have shown that the Cu clusters exhibit 'self-limiting' growth in the sense that with increasing coverage, the Cu cluster densities increase but the cluster sizes remain approximately constant. Our current studies of Cu grown on a partially reconstructed TiO@sub 2@(110)-(1x2) demonstrate that surface defects play an important role in determining the size and spatial distribution of the Cu clusters. Growth on the (1x2) surface is also 'self-limiting' and produces very uniform size distributions at all Cu coverages. However, the average cluster size at room temperature on the (1x2) surface (25Å diameter, 5Å height) is much smaller than on the (1x1) surface (~40Å diameter, 6-8Å height), and this difference is attributed to the decreased adatom mobility on the more defective (1x2) surface. Furthermore, the Cu clusters show no preference for residing at the titania step edges, which are the highest coordinate sites, even when the surface has been annealed to high temperatures (700-800 K) to increase the diffusion rate of the Cu adatoms. To further investigate this growth behavior, the initial stages of Cu cluster growth will be investigated by depositing Cu at low temperatures (25K-100 K) to prevent Cu adatom diffusion. The surface will then be heated to initiate adatom diffusion, and changes in the Cu clusters will be imaged by STM. We will also explore how the morphology of the Cu clusters is changed by oxidation at various temperatures. Both Cu deposition and oxidation studies can be performed during STM imaging.

SS1-ThP10 LITD-FTMS Study of Dehydrogenation of Cyclohexane on Al@sub 2@O@sub 3@-supported Pt Clusters*, **M.M. Ivey**, M.F. Luo, J.C. Hemminger,* University of California, Irvine

We present a study of the adsorption and subsequent thermally activated dehydrogenation of cyclohexane on oxide-supported Pt clusters by use of Fourier transform mass spectrometry (FTMS) in combination with laser-induced thermal desorption (LITD).@footnote 1@ Pt clusters were generated by thermal evaporation of Pt onto an Al@sub 2@O@sub 3@ ultra thin film of 10 Å thickness that was grown on a NiAl(001) surface through oxygen adsorption at high temperature.@footnote 2@ Both cyclohexane desorption and dehydrogenation are observed. The branching between the desorption and dehydrogenation paths was monitored using a combination of AES, TDS and LITD. The cyclohexane dehydrogenation on Pt clusters behaves in a manner significantly different from that on Pt(111) single crystal surfaces. We will show the reactivity/desorption behaviour for this system for a range of Pt surface loadings. This will be discussed in the light of the dependence on Pt average cluster size which was determined by an AES quantitative analysis of CO chemisorption, assuming hemispherical cluster shapes. @FootnoteText@ @footnote 1@ D.P. Land, C.L. Pettiette-Hall, J.C. Hemminger and R.T. McIver, Acc. Chem. Res. 24 (1991) 42. @footnote 2@ M.M. Ivey, H.C. Allen, A. Avoyan, K.A. Martin and J.C. Hemminger, J. Am. Chem. Soc. 120 (1998) 10980.

Surface Science
Room 134/135 - Session SS2-ThP
Beam Interactions with Surfaces Poster Session

SS2-ThP1 Evaluation of Surface Activity using a Molecular Probe*, **K. Iizumi**, K. Ueno, K. Saiki, A. Koma,* The University of Tokyo, Japan

It is important to investigate activity of various surfaces, since surfaces provide stages where various kinds of phenomena occur. We have examined to evaluate the surface activity through the interaction between C@sub 60@ and the surface. When the surface is active, the interaction between C@sub 60@ and the surface is strong. This strong interaction breaks the high symmetry of C@sub 60@ molecule and modifies its electronic structure. Then the electronic structure of adsorbed C@sub 60@

molecule indicates activity of the surface, onto which C@sub 60@ adsorb. In this sense, a C@sub 60@ molecule can be a good probe to know the degree of activity of the surface. In this paper, we chose three types of surfaces and estimated their activity. These three type of surfaces are as follows; (i) Si(111)-7x7 surface, (ii) dangling bond terminated Si(111) surface: Si(111)-@sr@3x@sr@3-Ag, Si(111)-@sr@3x@sr@3-Ga and Si(111)-1x1-As, (iii) layered material: MoS@sub 2@ cleaved surface. Monolayer C@sub 60@ films were grown on these surfaces and investigated electronic structures of C@sub 60@ by electron-energy-loss (EEL) spectroscopy in the reflection geometry. This is a powerful technique to study surface electronic structures of various materials. EEL spectra of C@sub 60@/Si(111)-7x7 and C@sub 60@/Si(111)-@sr@3x@sr@3-Ga are quite different from that of bulk C@sub 60@. On the other hand, EEL spectra of C@sub 60@/MoS@sub 2@ and C@sub 60@/Si(111)-1x1-As are the same as that of bulk C@sub 60@. The EEL spectrum of C@sub 60@/Si(111)-@sr@3x@sr@3-Ag resembles to that of bulk C@sub 60@. However there is small difference in peak intensities. As a result, we conclude that degrees of activity of above five surface are as follows: Si(111)-7x7, C@sub 60@/Si(111)-@sr@3x@sr@3-Ga >> Si(111)-@sr@3x@sr@3-Ag > C@sub 60@/MoS@sub 2@, C@sub 60@/Si(111)-1x1-As.

SS2-ThP2 Low-Energy Ion Scattering Study of Ag-Al Surface Composition@footnote 1@, ***R. Bastasz***, *J.A. Whaley,* Sandia National Laboratories*; W.P. Ellis,* Los Alamos National Laboratory

Diffusion and segregation effects have been examined for the Ag-Al system using the surface-specific technique of low-energy ion scattering (LEIS), which probes the outer atomic layer of materials.@footnote 2,3@ Thin (25 µm) foils of high-purity Ag and Al were placed in contact with each other and mounted on a heater assembly in a UHV chamber with the Al surface exposed. Initially LEIS signals from O and Al atoms were observed on the native oxide surface, but after cleaning by 1 keV He@super +@ bombardment only He@super +@ scattering from surface Al atoms was detected. The surface composition was then measured as a function of temperature up to 575 °C. No Ag was observed on the outer Al surface of Ag-Al foil samples heated to <500 °C. At 500 °C, prolonged heating resulted in the appearance of a LEIS signal from Ag at the Al surface. When the temperature of a fresh sample assembly was increased to near the eutectic (about 555 °C), the solids reacted rapidly to form a two-phase system@footnote 4@ and a LEIS signal from surface Ag immediately appeared. LEIS measurements of the surface composition of the clean binary system in the range 25-550 °C showed the Ag surface coverage to increase with temperature. Above the eutectic temperature, the Ag coverage decreased. Such LEIS measurements make it possible to determine the diffusivity of Ag in Al as well as the segregation enthalpy for Ag on Al surfaces. @FootnoteText@ @footnote 1@ This work was supported by the US Department of Energy under contract DE-AC04-94AL85000. @footnote 2@ E. Taglauer, in: "Surface Analysis- The Principal Techniques", J. C. Vickerman, Ed. (Wiley, 1997) Chap. 6. @footnote 3@ R. Bastasz, J. A. Whaley, and W. P. Ellis, Surf. Rev. Lett. 6 (1999) 605. @footnote 4@ A. J. McAllister and J. J. Murray, Bull. Alloy Phase Diagr. 1 (1983) 36.

SS2-ThP4 New Approaches to Diffusion and Electronic Properties of Surfaces: Spin-Echo Quasielastic Helium Scattering (SE-QHAS) and Metastable Helium Atom Scattering (MHAS), ***P. Fouquet***, Cavendish Laboratory, UK and MPI für Strömungsforschung, Germany, United Kingdom*; A.P. Jardine, J. Ellis, W. Allison,* Cavendish Laboratory, UK*; G. Witte,* Ruhr-Universität, Germany

We present current progress of two major new developments in atomic beam surface scattering: QHAS is a uniquely powerful technique for studying diffusion on atomic length and time-scales. Since helium atoms scatter from the diffusing species as they move, QHAS gives a detailed reciprocal space map of the paths the atoms take as they traverse the surface. We demonstrate the way that QHAS data can be used to study potential energy surfaces of diffusing atoms and adatom-adatom potential energies, as illustrated by analyses of experimental data on the CO/Cu(001) and Na/Cu(001) systems.@footnote 1@ Till now, QHAS has been limited to systems showing very high mobilities (D > 5 x 10@super -6@ cm@super 2@ s@super -1@), we show how measurements can be made over a much wider range of mobilities by using spin echo techniques and give details of a new ultra high resolution scattering machine that is being developed in the Cavendish. In contrast to that, metastable, excited He-atoms are highly sensitive to the surface electron density. We have shown experimentally that MHAS is capable of measuring the valence state occupation of alkali metals during growth on Cu(001).@footnote 2@ Our data interpretation has since found support by theoretical work which proved that, for the investigated systems, MHAS exclusively probes the electronic density of states projected onto the He 1s state.@footnote 3@ We have extended our measurements to alkaline earth metals (Ba), semiconductor surfaces (GaAs(100)) and oxygen coadsorption. The data supply novel information about the metallisation transition of ultrathin metal films as well as the catalytic oxidation of semiconductors. @FootnoteText@ @footnote 1@ J. Ellis, A.P. Graham, F. Hofmann, J. P. Toennies, Phys. Rev. B 63, 195408 (2001). @footnote 2@ P. Fouquet, G. Witte, Phys. Rev. Lett. 83, 360 (1999). @footnote 3@ L.N. Kantorovich et al., Surf. Sci. 444, 31 (2000).

SS2-ThP5 A Molecular Beam Study of Helium Absorption and Diffusion in Amorphous and Crystalline Ice, ***J.L. Daschbach***, *P. Ayotte, G.A. Kimmel, Z. Dohnalek, R.S. Smith, B.D. Kay,* Pacific Northwest National Laboratory

Molecular beam and thermal desorption techniques are employed to study the absorption and diffusion of He atoms in thin amorphous and crystalline ice films at low temperatures (20-100 K). The He absorption probability increases strongly with increasing translational energy (0.065 - 0.23 eV) and decreases dramatically as the incident angle is moved away from the surface normal (0-60°). These findings are indicative of a large activation barrier and a strong steric effect for the insertion of the He atoms into the bulk. Comparison between crystalline and amorphous ice suggests that absorption into the bulk occurs through hexagonal ring structures existing at the ice surface. Diffusion of He in ice is studied by growing ice films of varying thickness on top of a He impregnated ice substrate, and subsequently measuring the He permeation through the overlayer using temperature programmed desorption (TPD). The resultant He TPD data is analyzed using a coupled diffusion/desorption model to extract the temperature dependent diffusivity. The diffusion exhibits Arrhenius behavior with a diffusion barrier of 0.14 eV. The details of the experimental findings and their implications will be presented. @FootnoteText@ Pacific Northwest National Laboratory is a multiprogram National Laboratory operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

Surface Science

Room 134/135 - Session SS3-ThP

Surface Reactions Poster Session

SS3-ThP1 Thermal Behavior of NO on Stepped Pd(112), ***K. Irokawa***, *S. Ito, K. Okada, T. Okuya, H. Miki,* Science University of Tokyo, Japan

The thermal behavior of NO on a stepped Pd(112) surface has been investigated by ultraviolet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy(XPS) and Auger electron spectroscopy(AES). Ramsier et al. reported that at low coverage NO adsorbed molecularly at terrace sites on Pd(112) with the NO axis perpendicular to the terrace and as increasing the coverage NO adsorbed at step sites with the NO tilted to downstairs.@footnote 1@ It was found that four peaks appeared at 2.7, 9.4, 11.2 and 14.8eV below the Fermi level in a UPS spectrum, when the surface was saturated with NO at 300K.@footnote 2@ The peak appeared at 11.2eV originates from 1@pi@+5@sigma@ orbital of NO molecules adsorbed at the step sites of Pd(112) and the three remaining peaks originate from 2@pi@, 1@pi@+5@sigma@ and 4@sigma@ orbitals of NO molecules adsorbed at the terrace sites. The peak at 11.2eV vanished at 383K with increasing temperature, although the remaining peaks disappeared at 423K. This result indicates that an activity of NO dissociation at the step edge of the Pd(112) surface is much higher than the terrace. The N atoms desorbed from the surface at 700K. This behavior observed by UPS is consistent with results of XPS and AES. @FootnoteText@ @footnote 1@ R.D.Ramsier, K.-W.Lee and J.T.Yates,Jr., Surf. Sci. 322 (1995) 244. @footnote 2@ K.Irokawa, S.Ito, T.Kioka, H.Miki, Surf. Sci 433-435 (1999) 297.

SS3-ThP2 Simulation of Lateral Interactions in the Dissociation of NO on Rh(100) by Dynamic Monte Carlo Simulations, ***A.P. van Bavel***, *J.J. Lukkien,* Eindhoven University of Technology, The Netherlands*; J.W. Niemantsverdriet,* Eindhoven University of Technology, The Netherlands, Netherlands

The kinetics of the dissociation of NO on Rh(100) is largely determined by lateral interactions as a recent study using Temperature Programmed Desorption (TPD) and Temperature Programmed Static Secondary Ion Mass Spectrometry (TPSSIMS) by Hopstaken et.al.@footnote 1@ clearly shows. At zero coverage limit the NO dissociation is completed around 200 K. At increasing initial NO coverages the dissociation is retarded due to strong repulsions between NO and its decomposition products. At saturation coverage the NO dissociation is even fully retarded until a few NO molecules desorb from the surface, thereby creating the necessary vacancies for dissociation. The created vacancies are immediately filled with the atoms formed. This way an auto-catalytic process is developed, since the atoms cause more stronger repulsions and thereby more desorption. Due to the essential role of interactions and to the possibility of island formation, the kinetics cannot satisfactorily be described using a mean-field approach. Therefore, we have developed a model to describe the dissociation of NO on Rh(100) by means of Dynamic Monte Carlo simulations. We have included pairwise additive interactions between neighbouring species and diffusion of all adsorbates. Repulsion between NO and its decomposition products is larger than the mutual repulsion between NO molecules. This - in combination with the higher mobility of NO - leads to segregation in the adlayer to form mixed N@sub ads@+O@sub ads@ islands and compression of the NO in islands. The Monte Carlo simulations provide a means to estimate the magnitude of the interaction between neighbouring adsorbate species. @FootnoteText@ @footnote 1@ Hopstaken, M.J.P., Niemantsverdriet, J.W.; J. Phys. Chem. 104 (2000) 3058.

SS3-ThP3 Multi-directional N@sub 2@ Desorption in Thermal Dissociation of N@sub 2@O on Pd(110) and Rh(110) at Low Temperatures*, **H. Horino**,* Environ. Earth Sci. Hokkaido University, Japan*; T. Matsushima,* CRC, Hokkaido University, Japan

Multi-directional N@sub 2@ desorption was found in N@sub 2@O dissociation on Pd(110) and Rh(110) below 170 K by angle-resolved TDS. N@sub 2@ desorption sharply collimates off the surface normal in the (001) plane. Hot-atom-assisted N@sub 2@ desorption is proposed in aligned N@sub 2@O(a) dissociation. N@sub 2@O(a) is mostly dissociated during heating procedures, emitting N@sub 2@(g) and leaving O(a). N@sub 2@ showed four desorption peaks. Pd(110);@beta@@sub 1@-N@sub 2@ peaks around 150 K, @beta@@sub 2@-N@sub 2@ 134 K, @beta@@sub 3@-N@sub 2@ 123 K, and @beta@@sub 4@-N@sub 2@ 110 K. @beta@@sub 4@-N@sub 2@ was clearly seen at low N@sub 2@O exposures. It sharply collimated at ±50° off the surface normal. @beta@@sub 3@-N@sub 2@ was significant and revealed inclined sharp emission centered at ±43° off the surface normal. A similar distribution was also found with @beta@@sub 1@-N@sub 2@ found at high N@sub 2@O exposures, whereas @beta@@sub 2@-N@sub 2@ showed a cosine distribution. The preference of each N@sub 2@ peak was sensitive to pre-adsorbed O(a). Rh(110);@beta@@sub 1@-N@sub 2@ peaks at 165K, @beta@@sub 2@-N@sub 2@ 140 K, @beta@@sub 3@-N@sub 2@ 120 K and @beta@@sub 4@-N@sub 2@ 110 K. @beta@@sub 3@-N@sub 2@ and @beta@@sub 4@-N@sub 2@ collimated at @theta@=±33° and ±75°, respectively. These were seen at small exposures. @beta@@sub 1@-N@sub 2@ showed a cosine distribution. @beta@@sub 2@-N@sub 2@ desorption collimated at @theta@=±30°. Sharp inclined desorption possesses high kinetic energy. Prior to dissociation, N@sub 2@O(a) must lie on the surface. For inclined desorption, a surface parallel momentum must be transferred from nascent hot oxygen atoms to desorbing N@sub 2@. Larger inclined angles and higher kinetic energy may be expected on Rh(110) because higher hot-atom energy comes from the stronger metal-O bonding.

SS3-ThP4 Adsorption and Reaction of SO@sub 2@ with Cu(110) and Cu(110)-p(2x1)-O*, **A.R. Alemozafar**, X.-C. Guo, R.J. Madix,* Stanford University

Sulfur dioxide (SO@sub 2@) is infamous for its role as an environmental pollutant and in most circumstances a catalyst poison. Over the past twenty years SO@sub 2@ has been investigated on a number of single crystal metal surfaces, yet there is little SO@sub 2@/Cu(110) work. The results of our study which combines STM and TPRS to advance the understanding of the reactions of SO@sub 2@ on Cu(110) are reported. STM images reveal the formation of c(2x2), p(2x2) and c(4x2) surface structures when SO@sub 2@ interacts with the clean Cu(110) surface. The p(2x2) and c(4x2) structures form small domains, approximately 3-4 lattice units across, while the c(2x2) structures are considerably larger. The LEED pattern resulting from this reaction is a diffuse c(2x2), consistent with the domain sizes revealed by STM. STM studies of the dissociative adsorption of D@sub 2@S on Cu(110) reveal a c(2x2) sulfur structure on the surface with a corrugation identical to that observed upon SO@sub 2@ interaction with the Cu(110) surface, indicating that the c(2x2) moieties are due to sulfur adsorption. The p(2x2) and c(4x2) moieties are distributed randomly throughout the scan area in equal proportions, and STM shows similar corrugations of these two phases suggesting that they are the same SO@sub x@ species, stable up to 450 K (determined) by separate TPRS experiments. With the use of isotopic labeling the TPRS work suggests that the SO@sub x@ species is SO@sub 3@, with SO@sub 3@ bound to the surface via one of its oxygen atoms. This stoichiometry is consistent with the 1:2 ratio of the fraction of the surface covered by S and SO@sub x@ when the clean surface is exposed to SO@sub 2@. Further, from our STM images the binding site for the SO@sub 3@ can be determined to be a four-fold hollow. With our STM we have also probed the mobility of surface species. The real-time movie reveals the mobility of both SO@sub 3@ and oxygen rows along the [001] and [110] azimuths, respectively.

SS3-ThP5 NEXAFS Investigation of SO@sub 2@ Reactions on Oxygen-modified Ni (100) Surfaces*, **C.M. Kim**,* Kyungpook National University, Korea

The surface reaction of SO@sub 2@ and O on a Ni (100) surface has been investigated using a Near Edge X-ray Absorption Fine Structure (NEXAFS) technique and X-ray Photoelectron Spectroscopy (XPS). Four different surfaces were studied; clean Ni(100), p(2x2)_O/Ni(100), c(2x2)_O/Ni(100), and NiO(111)/Ni(100). Chemisorbed SO@sub 2@ was formed at 160 K on all four surfaces. Upon heating, SO@sub 2@ was decomposed to SO and atomic sulfur on clean Ni(100). On p(2x2)_O/Ni(100) and c(2x2)_O/Ni(100), however, SO@sub 3@ was formed in the temperature range of 200 to 400 K. Sulfur K-edge NEXAFS results showed that SO@sub 3@ was adsorbed with C3-axis perpendicular to the surface. On the NiO(111)/Ni(100) surface, both SO@sub 3@ and SO@sub 4@ were formed.

SS3-ThP6 Mechanism of O@sub 2@ Ejection from Pt(111) at 100K Induced by Gas-phase D Atom*, J.-Y. Kim, J.S. Choi, S.J. Lee, **J. Lee**,* Seoul National University, Korea

Rettner and Lee@footnote 1@ have shown that the gas-phase H(D) atom incident on an O2-adsorbed Pt(111) surface at 85K induces prompt desorption of O2 with a translational energy well in excess of the surface temperature. To elucidate the mechanism of this nonthermal desorption of O2, we have performed detailed kinetic studies using a D atom beam generated in a hot tungsten capillary tube at 1900K. Real-time monitoring of the gas-phase desorption products and post-reaction TPD measurements have been made with a QMS to find out 1) O2 and D2O desorb simultaneously with different kinetics, 2) the initial desorption rate of O2 is proportional to the O2 coverage, 3) at submonolayer O2 coverages, the O2 desorption rate increases with time following a step-like initial jump, which is more pronounced at a lower coverage, and 4) post-reaction TPD spectra show multiple D2O desorption peaks with increasing D atom exposure. Based on these observations, we conclude that O2 desorption occurs by site displacement of primary as well as secondary hot D atoms, which competes with D2O formation reaction. @FootnoteText@@footnote 1@ C. T. Rettner and J. Lee, J. Chem. Phys. 101 (1994) 10185.

SS3-ThP7 CO Adsorption on the c(2x2)-Mn/Cu(100) Surface Alloy: Magnetically Driven Restructuring*, **M. Grüne**,* Universität Bonn, Germany*; G. Boishin,* Universität Linz, Austria*; C. Becker, J. Breitbach, A. Frey, T. Pelster, K. Wandelt,* Universität Bonn, Germany

The c(2x2)-Mn/Cu(100) surface alloy is stabilized by the large magnetic moment of the Mn atoms yielding a substantial exchange energy.@footnote 1@ We have investigated the adsorption of CO on this alloy at 100 K by means of HREELS, UPS, LEED, and work function measurements. CO chemisorption passes through two subsequent stages. In no stage a CO-induced superstructure LEED pattern is seen. Initial adsorption of mainly side-on-CO, accompanied by adsorption at defects, leaves the substrate order intact. Subsequent adsorption of CO ontop Mn irreversibly destroys the long-range order of the substrate. This takes place by lateral interdiffusion, as can be shown by the application of UPS symmetry selection rules. We propose that the loss of the translational symmetry is related to a suppression of the local magnetic moment by ontop-CO adsorption. The reduction of the mnagnetic energy contribution causes a lifting of the energetic exclusion of Mn nearest neighbours, leading to a considerable entropy gain by lateral intermixing. @FootnoteText@ @footnote 1@see e.g.: M. Wuttig, Y. Gauthier, S. Blügel, Phys. Rev. Lett. 23 (1993) 3619-3622.

SS3-ThP8 The Adsorption and Dehydrogenation of Cyclohexane and Benzene on Pt Islands on ZnO(0001)-O*, A.W. Grant, **L.T. Ngo**, C.T. Campbell,* University of Washington

The dehydrogenation of perdeuterated cyclohexane and benzene on Pt/ZnO(0001)-O model catalysts were studied with temperature programmed desorption (TPD), ion scattering spectroscopy (ISS), and X-ray photoelectron spectroscopy (XPS). Pt grows as 2-dimensional (2D) islands on ZnO(0001)-O until they cover ~50% of the surface, and then 3D islands form. Thus, the reactivity of these Pt islands can be studied as a function of their thickness and lateral dimensions. On Pt(111), most of the adsorbed cyclohexane converts to benzene (> 300 K) decomposing to H@sub 2@ and adsorbed carbon. Two H@sub 2@ TPD peaks, at ~360K and ~540 K, are due to desorption of H lost in producing adsorbed benzene and C-H bond scission in benzene, respectively.@footnote 1@ Perdeuterated cyclohexane desorbs molecularly at ~200 K from Pt-free ZnO(0001)-O, and ~240 K from the Pt islands, where decomposition also occurs. The Pt island thickness affects the decomposition reaction of the resulting adsorbed hydrocarbons dramatically. @FootnoteText@ @footnote 1@ J. A. Rodriguez and C. T. Campbell, J. Phys. Chem. 1989, 93, 826-835.

SS3-ThP9 Acetylene on Cu(110): Trimerization and Chemical Bonding*, **H. Öström**, L. Triguero, K. Weiss, D. Nordlund, H. Ogasawara,* Uppsala University, Sweden*; L.G.M. Pettersson,* Stockholm University, Sweden*; A. Nilsson,* Uppsala University, Sweden and Stanford University, Sweden

We have studied the chemical bonding of acetylene on Cu(110) and the well known trimerisation reaction to benzene by high resolution X-ray photoelectron spectroscopy (XPS), near edge X-ray absorption fine structure (NEXAFS) spectroscopy and X-ray emission spectroscopy (XES). At liquid nitrogen temperature the XP spectra show two different C 1s peaks which correspond to two nonequivalent acetylene species adsorbed in different sites. By heating the sample, one species transforms into the other. This species disappears above room temperature due to the trimerisation of acetylene to benzene. We monitored the reaction with time resolved XPS, finding that benzene leaves the surface as soon as it is formed, in agreement with previous results. The adsorption geometry of the different adsorbate species have been determined by polarization dependent NEXAFS spectra, which shows that both species lie down on the surface, with different molecular alignment. XES shows that both species are chemisorbed on the surface with their electronic structure significantly distorted from the gas phase. The experimental results are completed by ab-initio cluster model calculations performed in the framework of density functional theory (DFT).

SS3-ThP10 Thermal Chemistry of cis-1,2-Dichloroethene on Pd(111)*, **D.M. Jaramillo**, D.E. Hunka, D.P. Land,* University of California, Davis

The decomposition of halogenated compounds on metal surfaces has generated significant interest due to the facile remediation of halocarbons by metal particles. Of particular importance are the reactions of toxic and/or carcinogenic compounds, such as chloroethenes. We have elucidated some mechanistic information about the decomposition of cis-1,2-dichloroethene on palladium. After adsorption on Pd(111) at 100 K, cis-1,2-dichloroethene thermally decomposed by 400 K to yield chlorine and hydrocarbon fragments. The only decomposition products observed by temperature programmed desorption (TPD) and laser-induced thermal desorption (LITD) were hydrogen chloride and hydrogen. Very little HCl was formed on the surface and only for exposures above 0.3 L. However, the presence of chlorine, observed by Auger electron spectroscopy (AES), on the surface above 650 K for exposures below 0.4 L indicates that decomposition occurred even though no HCl was observed. Possible surface intermediates were identified using Fourier transform reflection-adsorption infrared spectroscopy (FT-RAIRS).

SS3-ThP11 Adsorption of Cyclopentene and Cyclohexene on Ordered Sn/Pt(111) Surface Alloys*, **J. Breitbach**, D. Franke, G. Hamm, F. Jaeger, C. Becker, K. Wandelt,* University of Bonn, Germany

The adsorption of cyclopentene (C@sub 5@H@sub 8@) and cyclohexene (C@sub 6@H@sub 10@) on Pt(111) and two Sn/Pt(111) surface alloys has been investigated using HREELS, UPS, LEED and TPD. The two ordered Sn/Pt(111) alloys were prepared by annealing a Sn film deposited onto Pt(111). Depending on the temperature of annealing the surface exhibited a (2x2) or (@sr@3x@sr@3)R30° LEED pattern corresponding to a surface composition of Pt@sub 3@Sn and Pt@sub 2@Sn, respectively.@footnote 1@ At temperatures below 250K C@sub 5@H@sub 8@ and C@sub 6@H@sub 10@ adsorb intact on the pure Pt(111) surface. The di-@sigma@-bonding of the molecules is signified by the absence of the olefinic CH-stretching mode that is identified for the undisturbed molecules in the multilayer. Upon heating part of the C@sub 5@H@sub 8@ and C@sub 6@H@sub 10@ desorb and the remaining amounts are converted to C@sub 5@H@sub 5@ and C@sub 6@H@sub 6@, respectively. On the alloy surfaces the decomposition of C@sub 5@H@sub 8@ and C@sub 6@H@sub 10@ is completely suppressed. As the Sn concentration is increased, there is a marked decrease in the C@sub 5@H@sub 8@ desorption temperature from 278K on Pt(111) to 243K on the (2x2) alloy and to 192K on the (@sr@3x@sr@3)R30° alloy. This behaviour is in close analogy to the behaviour of ethylene on Sn/Pt(111)@footnote 2@ and hints to similar adsorption geometries of cyclopentene and ethylene on the pure Pt(111) surface. The adsorption of C@sub 6@H@sub 10@ is more dramatically influenced by alloying: On the (2x2) surface C@sub 6@H@sub 10@ is still di-@sigma@ bonded, while on the (@sr@3x@sr@3)R30° surface C@sub 6@H@sub 10@ is physisorbed. It can be concluded that C@sub 6@H@sub 10@ adsorbs on Pt-threefold hollow sites on Pt(111), which are not present on the (@sr@3x@sr@3)R30° surface. @FootnoteText@ @footnote 1@ M.T. Paffett, R.G. Windham Surf. Sci. 208 (1989) 34 @footnote 2@ Y.-L. Tsai, C. Xu and B.E. Koel Surf. Sci. 385 (1997) 37.

SS3-ThP12 Adsorption and Reaction of s-Triazine on Al(111)*, **V.J. Bellitto**, B. Bartlett, J.M. Valdisera, J.N. Russell, Jr.,* Naval Research Laboratory

Polycyanurates, cyanate ester resins with low-k-dielectric properties, are useful for the fabrication of microelectronic devices. Formed by the trimerization of monomers with cyanate functionalities, the polymer linkage in polycyanurates is a triazine ring. To understand how this linkage interacts with aluminum, a material used as interconnects in microelectronics, we examined the chemical interaction of 1,3,5-Triazine (C@sub 3@H@sub 3@N@sub 3@) and its isotopomer (C@sub 3@D@sub 3@N@sub 3@) on Al(111) using infrared reflection absorption spectroscopy (IRRAS), x-ray photoelectron spectroscopy (XPS), and temperature programmed desorption (TPD). A multilayer of triazine was produced by dosing the Al(111) surface while held at 140 K. Based on IRRAS measurements, triazine was randomly oriented in the multilayer. The multilayer desorption peak temperature occurred at 173 K, leaving a monolayer of triazine on the surface. At surface temperatures between 205 K and 300 K, similar IRRAS spectra were observed, showing modes at 1564 and 1341 cm@super -1@ and the absence of a mode at 737 cm@super -1@. Symmetry analysis of the IRRAS spectrum indicates the triazine molecular plane is tilted with respect to the Al(111) surface in the adsorbed monolayer, bonding through one of the nitrogen lone pairs. Thermal decomposition product desorption began around 425 K. HCN and H@sub 2@ desorption were observed, but surprisingly CH@sub 4@ and C@sub 2@H@sub 4@ desorption were also detected. Monitoring the decomposition products of C@sub 3@D@sub 3@N@sub 3@ confirmed the product assignments. Consistent with the desorption results, around 425 K the beginning of carbide and nitride formation was observed with XPS. Above 750 K, decomposition product desorption ceased. A broad phonon mode was observed at ~800 cm@super -1@ due to the formation of AlC@sub x@N@sub y@.

SS3-ThP13 The Chemistry of 1,1-Dichloroethene on Pd(111) Investigated by TDS, LITD-FTMS, STM and FTRAIRS*, **D.E. Hunka**,* University of California, Davis*; D.C. Herman,* University of North Carolina, Chapel Hill*; K.D. Lormand, A. Loui, S. Chiang, D.P. Land,* University of California, Davis

Chloroethene contamination in ground water is a concern from both an environmental and health standpoint. All six chloroethenes are contained in over half of the sites listed on the EPAâ€™s National Priorities List as well as possible carcinogens. One promising method of remediating these pollutants is using zero valent metals to degrade these halocarbons. Both iron and iron palladium bimetallic clusters have been shown to effectively decompose several small chlorocarbons, including dichloroethenes (DCEs). However, no systematic studies on palladium alone have been performed to date. In this study, the chemistry of 1,1-dichloroethene on clean Pd(111) has been investigated using thermal desorption spectrometry (TDS), laser induced thermal desorption Fourier transform mass spectrometry (LITD/FTMS), scanning tunneling microscopy (STM) and Fourier transform reflection absorption infrared spectroscopy (FTRAIRS). TDS and LITD-FTMS results indicate a coverage dependent decomposition mechanism. Coverages above 0.32 L show a stepwise decomposition initiated by C-Cl bond scission in which two successive stable surface intermediates are produced. These intermediates are proposed to be monochloroethylidyne and chlorovinylidene, respectively. The decomposition of 1,1-DCE in coverages below 0.32 L are initiated by C-H bond cleavage, and produce one stable surface intermediate, proposed to be dichloroethylidyne. All surface intermeidiates will be investigated and confirmed by FTRAIRS. Finally, STM reveals that adsorption and decomposition of 1,1-DCE happens preferentially at step edges.

SS3-ThP14 Structural Study on (CH@sub 3@)@sub 2@S/Cu(100) by Near Edge X-ray Absorption Fine Structure and X-ray Photoelectron Spectroscopy, ***S. Yagi,*** Nagoya University, Japan

Adsorption behavior of a molecule on metal surface has been interested in a catalytic and surface reaction fields. In this study, we have studied an adsorption structure of the (CH@sub 3@)@sub 2@S on Cu(100) surface by use of polarization dependent S K-edge Near Edge X-ray Absorption Fine Structure (NEXAFS) and S 1s X-ray Photoelectron Spectroscopy (XPS) techniques. The Cu(100) crystal was cleaned by means of the Ar@super +@ bombardment and annealing up to 800 K. The cleanliness and order of the surface were verified by XPS and LEED. Research grade (CH@sub 3@)@sub 2@S molecule was introduced with an exposure of 0.4 L to the Cu(100) at 90 K, in order to obtain a submonolayer phase. S K-edge NEXAFS and XPS measurements were carried out at the soft X-ray double crystal monochromator beamline BL-3 on Hiroshima Synchrotron Radiation Center. By comparing the edge-jump ratio between the submonolayer phase and the S atomic adsorption phase, the S amount was estimated to be 0.2 ML. Noticeable polarization dependence can be seen in the NEXAFS spectra, first feature (1s-@sigma@@super *@(S-C)) is enhanced at normal incidence (electric vector is parallel to the surface). This result imply that the (CH@sub 3@)@sub 2@S molecule is lying on the Cu(100) surface without the cleavage of the S-C bonds. A significant chemical shifts of the S 1s XPS peak were observed to a lower binding energy side in the submonolayer phase compared to that of the multilayer. It found that the charge transfer occurs from the substrate to the S atom of the molecule.

SS3-ThP16 Reactions of Perchlorate on Titanium/Titanium Oxide Surfaces Studied by LITD/FTMS., ***K.D. Lormand,*** *D.E. Hunka, D.P. Land,* University of California, Davis

Organic contaminants in water supplies have been a concern for decades, due to possible deadly health effects. Perchlorates, in particular, have posed a major concern as of late due to their irreversible and damaging affects on the human thyroid,@footnote 1@ long residence time in water sheds, and resistance to existing catalysts used in water treatment.@footnote 2@ Catalysts, such as palladium, iron, and platinum, have been found to be quite effective in reducing the concentration levels of most halocarbon residues, but are ineffective on perchlorates. However, preliminary studies of oxidized surfaces of titanium exposed to ultraviolet radiation have been seen to reduce perchlorates in aqueous solutions effectively. Reaction mechanisms of many halocarbon residues on palladium and platinum catalysts have already been elucidated using laser induced thermal desorption and conventional thermal desorption with FT mass spectrometry (LITD/FTMS) on clean surfaces in ultra high vacuum (UHV). Though these studies reveal accurate reaction mechanisms, they are done in an ultra clean environment and do not fully incorporate atmospheric gases into the equation. We have recently designed a new LITD/FTMS chamber to allow the rapid introduction of samples from reaction in aqueous solution into UHV for analysis. This allows for more inclusive reaction mechanisms to be determined due to the incorporation of atmospheric water and oxygen. The reaction of perchlorate is investigated on both titanium metal as well as titanium oxide using LITD/FTMS. While titanium itself is less reactive, the oxides show increased activity and studies of varying oxide layers are presented. @FootnoteText@ @footnote 1@ Siglin, J.C.; Mattie, D.R.; Dodd, D.E.; Hildebrandt, P.K.; Baker, W.H. Toxicol. Sci. 2000, 57(1), 61-74. @footnote 2@ http:/www.epa.gov/ogwdw000/ccl/perchlor/perchlo.html .

SS3-ThP17 Surface-Termination-Dependence of the Reactivity of Single Crystal Hematite with Carbon Tetrachloride, *N. Camillone III, K. Adib, K.T. Rim, J.P. Fitts, G.W. Flynn,* Columbia University; *S.A. Joyce,* Pacific Northwest National Laboratory; ***R.M. Osgood, Jr.,*** Columbia University

We describe ultrahigh vacuum Auger electron spectrometric measurements of the uptake of chlorine following the exposure of single crystal hematite to CCl@sub 4@ at room temperature. We compare the surface chemistry of two distinct terminations of @alpha@-Fe@sub 2@O@sub 3@: the Fe@sub 3@O@sub 4@ "selvedge" and the @alpha@-Fe@sub 2@O@sub 3@ / FeO "biphase." For Fe@sub 3@O@sub 4@ (111)-2x2 we estimate that saturation levels of Cl of at least ~ 27 % of a monolayer are attained at relatively low exposures of on the order of 0.1 L. No significant amount of carbon uptake is detected. Low energy electron diffraction measurements suggest that, dependent upon preparation procedures, at least two types of @alpha@-Fe@sub 2@O@sub 3@ / FeO biphase structures can be formed. Interestingly, no significant Cl or C adsorption is detected for either of these biphases, revealing a marked difference in the reactivity of the terminations. Comparison of these results with the surface structure of these terminations suggests that the active site for the dissociative adsorption of CCl@sub 4@ on Fe@sub 3@O@sub 4@ (111)-2x2 must comprise both an iron cation and an oxygen anion that is uncapped by iron cations. Modification of the biphase termination by thermal treatment, as well as the electron-stimulated and thermal desorption of Cl from the saturated Fe@sub 3@O@sub 4@ (111)-2x2 selvedge will be discussed. Finally, the relationship between these results and our recent STM measurements on this system will be presented.

SS3-ThP18 Optical and STM-based Excitation of Adsorbed Molecules, ***L. Bartels,*** University of California at Riverside; *D. Moeller, T.F. Heinz,* Columbia University; *E. Knoesel,* Rowan University; *G. Meyer, S.W. Hla,* Free University Berlin, Germany; *A. Liu,* University of California at Riverside; *K.H. Rieder,* Free University Berlin, Germany

Optical and STM-based excitation of adsorbed molecules Photodesorption and other photochemical reactions have been studied for a long time. Using femtosecond lasers, lately minute details of such surface reactions could be revealed that result in desorbing species. Simultaneously, scanning tunneling microscopy has matured from a pure imaging technique to a highly precise and powerful adsorbate and surface manipulation tool. Here experiments are shown, in which the diffusion of individual adsorbed molecules is induced by electron attachment from an STM tip and by optical excitation. In both cases the resultant diffusive motion on the surface is measured by STM. In both cases diffusion pattern are found, which do not occur under equilibrium thermal conditions.

SS3-ThP19 A Comparative Study of the Adsorption of Acetylene, Ethylene and Benzene on the Pure Pd(111) Surface and the Ordered Pd@sub 2@Sn Surface Alloy on Pd(111), ***G. Hamm,*** *T. Schmidt, J. Breitbach, D. Franke, C. Becker, K. Wandelt,* University of Bonn, Germany

The adsorption of acetylene, ethylene and benzene on the pure Pd(111) surface and the ordered Pd@sub2@Sn surface alloy on Pd(111) has been investigated with TPD, LEED, UPS and HREELS. The surface alloy with (@sr@3 x @sr@3)R30° periodicity corresponding to the Pd@sub 2@Sn composition was produced by annealing of multilayer amounts of Sn vapor deposited onto Pd(111).@footnote 1@ Below 300K benzene chemisorbs intact on the pure Pd(111) surface, bonding via its @pi@-electron system. In the range 300-500K most of the adsorbed benzene desorbs while a small part is dehydrogenated leaving a CCH species on the surface. For the first time an ordered superstructure of benzene has been found at room temperature. On the alloy, benzene can only be physisorbed. Ethylene is most probably di-@sigma@ bound on the pure Pd(111) surface below 250K, whereas ethylidyne is the dominant species after the adsorption of ethylene at 350K. In the temperature range from 150 to 300K most of the ethylene desorbs. At the same time part of the molecules undergo a three step conversion into ethylidyne above 250K. Due to the absence of appropriate conversion sites and the weak adsorption, this reaction is totally suppressed on the alloy. Acetylene chemisorbs on both surfaces. While the electronic structure of the adsorbed molecule is nearly identical on the pure Pd(111) surface and the alloy, vibrational spectroscopy reveals marked differences. Benzene is reactively formed from adsorbed acetylene on pure Pd(111), exhibiting two desorption peaks at 200K and 500K, which are ascribed to tilted and flat lying benzene. The majority of the acetylene is, however, converted to ethylidyne near room temperature via a vinylidene intermediate. In contrast to Pd(111), both reactions are suppressed on the alloy surface resulting in a single acetylene desorption peak at about 160K. @FootnoteText@ @footnote 1@ A. F. Lee, C. J. Baddeley, M. S. Tikhov, R. M. Lambert, Surf. Sci. 373 (1997) 195.

Surface Science

Room 134/135 - Session SS4-ThP

Semiconductor Morphology Poster Session

SS4-ThP1 Surface Stress of Thin Epitaxial CaF@sub 2@ Films on Si(111), *P. Zahl, A. Klust,* ***M. Bierkandt,*** *J. Wollschläger,* Universität Hannover, Germany; *M. Horn- von Hoegen,* Universität GH Essen, Germany

In this paper we present the first elastic properties characterisation of ultrathin epitaxial grown calcium fluoride films (thickness up to five molecular layers) using SSIOD (Surface Stress Induced Optical Defection@footnote 1@). This experimental technique will be explained and demonstrated by Hydrogen ad-/desorption on Si(111). From the large difference in thermal expansion coefficients@footnote 2@ between CaF@sub 2@ and Si a change in volume misfit from 0.5% at room temperature up to 2.5% at 1000 K takes place. The analysis of stress increase during growth at different temperatures (e.g. misfits) allows estimating the stress at the Si/CaF@sub 2@ interface. A change of the surface reconstruction at approx. 900K between 1 and 3 TL is detectable by SSIOD. Furthermore, the measurements are showing, that although at 600K a relaxed and stress free thin films can be grown, a volume lattice misfit of approx 1.5% exists. @FootnoteText@ @footnote 1@ P. Zahl, "Oberflächenspannung auf Si(111): Heteroepitaxie von Ge und CaF@sub 2@, Adsorption von H und Sb", Logos Verlag Berlin 2000, ISBN 3-89722-571-9 @footnote 2@ M. A. Olmstead, in: Thin Films: Heteroepitaxial Systems, Chapter: "Heteroepitaxy of Strongly Disparate Materials: From Chemisorption to Epitaxy in CaF@sub 2@/Si(111)", pp. 211-266. World Scientific Publishing, Singapore, 1999 @footnote 3@ Ohmi, S. K. Tsutsui, S. Furukawa; Jpn. J. Appl. Phys., 33:1121, 1994 @footnote 4@ J. Wollschläger, A. Klust, H. Pietsch; Appl.Surf.Sci., 123/124:496-500, 1998.

SS4-ThP2 STM Investigation of Sn,Pb/Si(111)-(3x3) Phase at RT and LT*, **H. Morikawa**, K. Horikoshi, S. Hasegawa,* University of Tokyo, Japan

Pb,Sn/Ge(111) surfaces are well known systems for their 'phase transitions' from room-tenperature(RT) @sr@3x@sr@3 phases to low-temperature(LT) 3x3 phases. However, relatively few investigations have been made for the Pb, Sn/Si(111) systems.@footnote 1@ We have made STM studies for these surfaces both at RT and LT (70K). Although a long-range ordered 3x3 phase does not appear in STM images at LT in the Sn/Si system, we could see an apparent 3x3 domains for the Pb/Si system around defects. Only in the case of Pb/Si, defects aligns to form the 3x3 periodicity. In these systems, defects are important for inducing the 3x3 order. We investigated the defect-defect correlation for both sytems, in relation with the 'Defect Density Wave'on the Sn/Si(111).@footnote 2@ Furthermore we found @sr@3x@sr@3(RT) and 3x3(LT) islands for Pb/Si, which was not seen in the Sn case. @FootnoteText@ @footnote 1@K Horikoshi, et al,Phys.Rev.B 60,13287 (1999) @footnote 2@L Ottaviano,et al,Phys.Rev.Lett.86,1809(2001).

SS4-ThP3 High-Temperature Phase Transitions on the Si(111) Surface*, **C. Jeon**,* Sung Kyun Kwan University, Korea*; C.C. Hwang, K.-J. Kim, T.-H. Kang, B. Kim,* Pohang Accelerator Laboratory, Korea*; C.Y. Park,* Sung Kyun Kwan University, Korea

Surface melting of semiconductors has been widely studied up to now. Recent theoretical@footnote 1@and experimental@footnote 2@ results suggest that the Si(111) surface undergoes an incomplete melting at high temperature below the bulk melting point (1680 K). In this work, angle resolved ultra-violet photoemission spectroscopy was performed to investigate the phase transitions on the Si(111) surface with rising temperature from room temperature (RT) up to 1600 K. By analyzing of the integrated emission intensity at the Fermi level, we observed a change of metallic character as a function of temperature.@footnote 3@ As previously reported, the Si(111) 7x7 surface has metallic nature at RT. A linear increase with temperature and an abrupt rise of the intensity at the critical temperature (Tc=1100K) is observed. At the same time, the Si(111) surface structure transforms from the (7x7)-DAS to the high temperature 1x1 structure. At 1470 K, the decrease in its metallicity shows the presence of another phase transition taking place at about 200 K below the bulk melting point. Based on these results, we'll discuss the origin of the two phase transitions on the Si(111) surface at elevated temperatures. @FootnoteText@ @footnote 1@ A. Natori, T. Suzuki, and H. Yasunaga, Suf. Sci. 367, 56 (1996) @footnote 2@ Y. Fukaya and Y. Shigeta, Phys. Rev. Lett. 85, 5150 (2000) @footnote 3@ I. Stich, R. Car, and M. Parrinello, Phys. Rev. Lett. 63, 2240 (1989)

SS4-ThP4 Thermal Decay of Isolated Single Silicon Mounds on the Si(100)-(2x1) Surface*, **S. Nishida**, A. Ichimiya,* Nagoya University, Japan

We have studied the decay process of a silicon mound on the Si(100)-(2x1) surface at 500°C. The mound has been fabricated by an STM tip. The shape of the mound is a quadrangular pyramid with facets of regular array of steps that have double layer height. For the all step, the dimer rows are perpendicular to the step edges, so called the D@sub B@ step. Just after fabrication, the pyramid begins to decay layer-by-layer. During the decay, area of the bottom single layer of the pyramid is grown toward the dimer row direction. The layer width does not change toward perpendicular to the dimer rows. The area of the topmost layer of the pyramid decreases toward perpendicular to the dimer rows, because the both S@sub B@ step edges are pinned by the step edges of the lower ones. Therefore the D@sub B@ step edges remain at the each step edge, and move scarcely. But only the S@sub B@ steps at the bottom layer move due to attachment and detachment of atoms which are detached from the upper layers. The decay process of a single layer mound on the Si(100) surface is very different from that of the topmost layer of the pyramid. The S@sub B@ steps fluctuate greatly. Roughness of the S@sub B@ steps changes periodically. The aspect ratio of the mound oscillates between about 2.5 and 1.5. The decay rate of a single layer mound varies with each mound. The rate is affected by the defect of the surface. The increase of the defect ratio causes the decrease of the decay rate.

SS4-ThP5 Growth of Cu on Si(5 5 12)*, **P.H. Woodworth**, J.C. Moore, J.L. Skrobiszewski, A.A. Baski,* Virginia Commonwealth University

We have used scanning tunneling microscopy (STM) to study the growth behavior of Cu on the row-like surface of Si(5 5 12). Our prior work concerning noble metal growth (Au, Ag) on this surface has shown a variety of row-like overlayer structures and Au-stabilized facet planes.@footnote 1@ This study compares and contrasts the growth behavior of Cu to its counterparts. At very low coverage (<0.1 ML) and moderate annealing temperatures (600°C), Cu induces faceting of the (5 5 12) surface to the nearby (337) and (5 5 13) planes, neither of which is a stable clean Si surface. Faceting to (337) has also been observed for low-coverage Au deposition, indicating a similarity between these two metals. In contrast to both Au and Ag growth, however, Cu is not seen to form row-like overlayer structures on the basal Si(5 5 12) surface. At higher coverages up to one monolayer, Cu causes the surface to form sawtooth facets comprised of (113) and (111) planes, where an ordered (113)2x2 reconstruction is observed. Interestingly, a large number of domain boundaries form between the 2x2 regions, resulting in a "weave-like" pattern of short rows. The stabilization of the (113) plane by metal deposition on (5 5 12) has also been observed for Au, Ag, and Sn deposition, but the 2x2 reconstruction is unique to Cu. Results for Cu deposition on (113) to produce the 2x2 phase will also be presented. @FootnoteText@ @footnote 1@ A.A. Baski, K.M. Jones, K.M. Saoud, Ultramicroscopy 86 23 (2001).

SS4-ThP6 LEED I-V Curve Analysis of Adsorption Structures of Ba on Si(001) Surface*, **T. Urano**, Y. Takeda, S. Hongo,* Kobe University, Japan

Ba atoms adsorbed Si(001) surfaces show 2x3, c(2x6), 2x1 and 2x4 superstructures at submonolayer coverage, successively.@footnote 1,2@ These structures have been examined by LEED I-V curve analysis. The genetic search algorithm proposed by Doll and Van Hove@footnote 3@ has been operated to find a global optimum structure efficiently. After that the automated Tensor LEED analysis is carried out to refine the structure more precisely. Several structure models have been proposed by other researchers.@footnote 4@ In our previous LEED observation using a single domain Si(001)2x1 substrate, the direction of the two-fold periodicity of the 2x4 and 2x3 structures was determined to be parallel to the Si dimer.@footnote 1@ For the 2x3 structure, several models having Ba atoms of 1/6 monolayer(ML) and 1/3 ML, which is consistent with the UPS results showing the existence of dangling bond and dimer bond states, have been considered. The results of STM observations@footnote 5@ have been also considered. At the moment, though the R-factor value is not small enough, the model in which Ba atoms sit on the 3rd layer substrate Si atoms is most suitable. For the 2x1 and 2x4 structures, an amount of Ba atoms in the models are 1/2 and 1 ML, respectively. These results will be shown in the conference. @FootnoteText@ @footnote 1@Y.Takeda et.al.,Surf.Sci.402-404(1998)692. @footnote 2@X.Hu et.al.,Surf.Sci.426(1999)69. @footnote 3@R.Doll and M.A.Van Hove, Surf.Sci.355(1996)L393. @footnote 4@W.C.Fan and A.Ignatiev, Surf.Sci.253(1991)297. @footnote 5@K.Ojima, submitted to Surf.Sci.

SS4-ThP7 High Resolution AES Mapping and TEM Study of Cu(In,Ga)Se@sub 2@ Thin Film Growth*, **C.L. Perkins**, Y. Yan, K.M. Jones, R. Noufi,* National Renewable Energy Laboratory

The chalcopyrite Cu(In,Ga)Se@sub 2@ (CIGS) shows promise as an absorber layer in thin polycrystalline solar cells, however, many details of this complicated material's growth processes remain unclear. At one point during the so called "three stage" CIGS growth process used at the National Renewable Energy Laboratory (NREL) and elsewhere, the growing film is subjected to a copper rich flux in a selenium ambient. Previous workers have postulated that during this stage there exists a thin film of liquid Cu@sub x@Se at the outermost portion of the CIGS, and that this layer acts as a reservoir of copper as well as a layer in which rapid mass transport is possible. In this paper we present TEM and high resolution AES mapping data taken on samples that had their growth interrupted at a stage when Cu@sub x@Se was expected to be present. The AES maps show CIGS grains which are highly enriched in copper relative to the rest of the CIGS film, and that these same areas contain almost no indium, results consistent with the presence of Cu@sub x@Se. Small area diffraction analysis and energy dispersive spectroscopy (EDS) performed on these same samples independently confirm the presence of Cu@sub x@Se at the surface of growing CIGS films. The implications of these results are discussed in terms of the efficiencies of CIGS photovoltaic devices.

SS4-ThP8 Surface Structures of SiC(0001) Surfaces and Oxygen Adsorption Effects*, **T. Aoyama**, A. Ichimiya,* Nagoya University, Japan*; Y. Hisada, S. Mukainakano,* Denso Corporation, Japan

Surface structures of SiC(0001) @sr@3x@sr@3 R30° and 3x3 surfaces have been studied by rocking curves of reflection high energy electron diffraction (RHEED) intensities and auger electron spectroscopy (AES). The @sr@3x@sr@3 reconstruction is observed by annealing the Si pre-deposited specimen in a Si flux at 1000°C for 5 min. The 3x3 reconstruction is observed by successive annealing the @sr@3x@sr@3 surface in a Si flux at 940°C for 5 min. It is obserbed on the auger spectrums of @sr@3x@sr@3 and 3x3 surfaces that Si LVV peak of the @sr@3x@sr@3 is located at kinetic energy of 87 eV and that of the 3x3 surface is located at 91 eV. From the peak to peak ratio of Si LVV to C KLL of these surfaces, it is considered that the 3x3 is Si-rich surface (the ratio: 3) and the @sr@3x@sr@3 surface is Si-poor (the ratio: 0.6). From the structural analysis with RHEED dynamical calculations, it is concluded that the @sr@3x@sr@3 surface is terminated with C trimers on T@sub 4@ or H@sub 3@ sites and the 3x3 surface is terminated with Si pyramidal clusters. Oxygen adsorption effects on the 3x3 surface have been also studied by RHEED and AES. After 10@super 5@ L (1.5x10@super -4@ Torr, 15 min) oxygen exposure at 1000°C on the 3x3 surface, the RHEED pattern changes to 1x1 periodicity and the peak to peak ratio of Si LVV to C KLL and Si LVV to O KLL becomes 0.5 and 0.8, respectively. It is estimated that about 1/3 ML of oxygen atoms are adsorbed on the surface. From the AES results, it is considered that the oxygen atoms are located on embedded sites.

SS4-ThP9 Surface Morphology of CuInS@sub 2@ Thin Films*, **A. Azuma**, Y. Akaki, H. Komaki, T. Ikari,* Miyazaki University, Japan

Solar cell techniques using I-III-VI@sub 2@ chalcopyrite semiconductors have made rapid progress for the solution of environmental and resources problems. Among chalcopyrite semiconductors, CuInS@sub 2@ may be the most promising material for photovoltaic applications due to the bandgap energy of 1.5 eV which perfectly matches the solar spectrum for energy conversion. However, the physical properties of CuInS@sub 2@ are almost unknown.In this work, the CuInS@sub 2@ thin films were grown by vacuum evaporation method. The source material was CuInS@sub 2@ compound material grown by Hot-Press method. Using substrate was glass and growth temperature is room temperature. After the vacuum evaporation, the sample was annealing under Ar or air atmospheres from 200 to 500 °C. The samples were examined by X-ray diffraction (XRD), electron probe microanalysis (EPMA), scanning electron microscopy (SEM) and optical absorption measurements.The XRD spectra indicate that poly CuInS@sub 2@ films are successful grown on glass substrate until 300 °C. CuIn@sub 5@S@sub 8@ and Cu@sub 2@S are grown with increasing the annealing temperatures. The EPMA results are in good agreement with the stoichiometry compositions of the CuInS@sub 2@, CuIn@sub 5@S@sub 8@ and Cu@sub 2@S films. Surface Morphology of the samples is drastically changed. A number of the spots increase with increasing the annealing temperatures. Furthermore, absorption coefficients decrease with increasing the temperatures.

SS4-ThP10 Atomic Resolution Imaging of Si(100)1x1:2H Dihydride Surface with Non-contact AFM*, **S. Araragi**, Y. Sugawara, S. Morita,* Osaka University, Japan

Noncontact atomic force microscopy (NC-AFM) is a useful tool which has an atomic resolution applicable to many fields such as surface science. It is very important to understand the interaction on hydrogen atoms and silicon surface, when we deepen the knowledge as the surface treatment and semiconductor materials of a nano scale. Therefore, the hydrogen terminated silicon surfaces have been actively studied as the most important fields of surface physics. In the previous experiment, we succeeded in the NC-AFM imaging of individual hydrogen atom on the Si(100)2x1:H monohydride surface. Thus, the NC-AFM is suitable for the observation of the hydrogen terminated silicon surface. In this paper, we investigate how the NC-AFM images the Si(100)1x1:2H dihydride surface. As a force sensor, we used a clean silicon tip. The image with the 1x1 structure was observed when the tip was relatively far from the sample. When the distance between the tip and the sample became closer, the 2x1 structure where the bright line and the dark line were alternately located was observed. Furthermore, when the tip became closer, the 1x1 structure was again appeared. It is considered that the attractive interactions between the tip and the sample changed with the change of the distance between the tip and the sample. When the tip is relatively far from the sample, the 1x1 structure of the original dihydride surface is imaged because of less the attractive interaction. However, when the tip approaches the sample, the attractive interaction between the tip and the sample becomes stronger and hence the structure of dihydride surface changes. It turns out that the Si(100)1x1:2H dihydride surface changes by the attractive interaction between the tip and the sample in NC-AFM.

Thin Films
Room 134/135 - Session TF-ThP
Thin Film Deposition/Carbon-Containing Films Poster Session

TF-ThP1 Substrate Response During Dual Bipolar Pulsed Sputtering*, P.J. Kelly,* University of Salford, U.K., UK*; J. O'Brien,* University of Salford, U.K., England*; J.W. Bradley,* UMIST, U.K.*; **P.S. Henderson**,* University of Salford, U.K., UK*; R. Hall,* Advanced Energy Industries UK Ltd.

Dual bipolar pulsed sputtering is a highly successful technique for the deposition of dielectric materials. Operating in the mid-frequency range (20-350kHz), each magnetron acts alternately as an anode and a cathode. With the polarity of each magnetron alternating in this manner, target cleanliness is maintained, anode surfaces are preserved, and long term process stability is achieved. Asymmetric bipolar pulsed DC power supplies are commonly used to drive this process. In such instances, the target voltage during each pulse-off period typically reverses to approximately 10% of the nominal pulse-on voltage, i.e., if the pulse-on voltage is â€“400V, then the pulse-off voltage will be approximately +40V. However, as pulse frequencies are increased, particularly to in excess of 150kHz, target voltage waveforms increasingly depart from this idealised "square wave" behaviour. Very significant voltage overshoots are observed in each direction during each half of the pulse cycle. In particular, large positive overshoots are observed at the beginning of each pulse-off period. For example, at a pulse frequency of 350kHz, the target voltage can reach a peak value of +500V. Monitoring of the substrate I-V waveforms during operation has revealed that similar transient "spikes" also occur here. As a result, there is a short burst of high energy ions incident at the substrate during each "spikes", and since two targets are in use, these transients occur at twice the pulse frequency. Clearly, such bursts of high energy bombardment could have a significant influence on the growing film. Consequently, an investigation into the complex processes occurring at the substrate during dual bipolar pulsed sputtering has been carried out. A model is proposed to account for the observed phenomena, and the impact on film properties is considered.

TF-ThP2 Modified HFCVD System for Diamond Coatings on Dental Burrs*, H. Stein, **W. Ahmed**,* Manchester Metropolitan University, U.K.*; C.A. Rego, N. Ali,* Manchester Metropolitan University, U.K., UK

Chemical vapour deposited diamond films grown in a modified hot filament reactor using filament metals such as tantalum and tungsten have been optmised. The non-planar e.g. a small dental burrs or small metal abrading device was used as a substrate. The filament in hot filament chemical vapour deposition "HFCVD" plays an essential role in creating the gas phase species that enable and influence the diamond growth. The modification of HFCVD was such that the coiled filament was fixed vertically within the vacuum deposition chamber as opposed to horizontal position as used in conventional HFCVD systems. The dental burrs were placed within the coiled filament during deposition and this was the distinctive feature of the system. The substrate varied from 0.5mm to 1.25mm in diameter and were as long as 20mm. The as-grown diamond films were found to be polycrystalline, uniform and the film coverage was good. A preferential diamond (111) surface morphology has been obtained which is srongly dependent on diamond growth paramaters, including substrate and filament position in the reactor. Raman spectroscopy and scanning electron microscopy measurements confrimed the good quality of the obtained diamond films.

TF-ThP3 High Rate Deposition of Thick CrNx Films by Unbalanced Magnetron Sputtering*, **K.H. Nam**, J.H. Bin, J.G. Han,* Sungkyunkwan University, Korea

The high rate deposition processes such as high current arc, laser arc, hollow cathode discharge ion plating and magnetron sputtering method have been developed for cost effective industrial applications. Especially magnetron sputtering is emerging a very efficient method for high rate deposition of dense thin films. In previous works, we have synthesized CrNx films by magnetron sputtering. The deposition rate was reached to be about 0.6µ/min. and the microhardness was evaluated up to 2200kg/mm2. And then phase and microstructure were controlled by change of N2 partial pressure and pulsed DC bias. In this study, high rate deposition of thick CrNx films was carried out by magnetron sputtering for the special application such as piston ring employed in automobile engine. For the high rate deposition of CrNx films with thickness of 30µ, residual stress in films was controlled by various N2 partial pressure, target power density and bias in processing. The microstructure was analyzed by X-ray Diffraction(XRD) and Scanning Electron Microscopy(SEM) and mechanical properties were evaluated by microhardness test, residual stress and adhesion tests.

TF-ThP4 Comparison of Poly-Si Films Deposited by UHVCVD and LPCVD and Its Application for Thin Film Transistors*, D.Z. Peng,* *H.W. Zan,* National Chiao Tung University, Taiwan*; T.C. Chang,* National Sun Yat-Sen University, Taiwan, Taiwan, R.O.C.*; C.Y. Chang, P.S. Shih,* National Chiao Tung University, Taiwan

The ultra high vacuum chemical vapor deposition (UHV/CVD) system can deposite poly-Si film without any laser or furnace annealing at lower temperature (550C). The uniformity of threshold voltage and mobility is superior to that deposited by low pressure chemical vapor deposition (LPCVD) system. The threshold voltage and mobility deviation for UHV/CVD are 0.16V, 10%, respectively and 0.23V, 21% for LPCVD system. However, due to the deposition in polycrystalline phase for UHV/CVD, the film surface is rough and results in low field effect mobility (27 cm2/VS, after plasma passivation, p-type device) compared to that (103 cm2/V-s, after plasma passivation, p-type device) obtained by low pressure chemical vapor deposition (LPCVD) using disilane (si2H6) in amorphous phase followed by solid phase crystallization (SPC). It can be shown that poly-Si film thickness will influence the leakage current. In this thesis, NH3, N2 and N2O were used to passivate the devices. They have obvious improvement on device performance after plasma passivation, in addition, NH3 passivation will result in the smallest leakage currrent and highest on/off current ratio. However, N2O needs a longer passivation time compared to the other two. After passivation, the devices show a poor stress endurance compared to unpassivated devices.

TF-ThP5 Oxygen Partial Pressure Effect on the Properties of the Novel Semiconducting Alloy Cu@sub x@Cd@sub 1-x@Te Grown by rf Sputtering*, J. Santos-Cruz,* ***G. Torres-Delgado****, O. Jiménez-Sandoval, R. Castanedo-Pérez,* Cinvestav-IPN, Unidad Querétaro, Mexico*; B.S. Chao,* Energy Conversion Devices, Inc.*; P. García-Jiménez, S. Jiménez-Sandoval,* Cinvestav-IPN, Unidad Querétaro, Mexico

High quality thin films of the novel semiconductor alloy Cu@sub x@Cd@sub 1-x@Te have been succesfully grown by rf sputtering from a single target made of a mixture of high purity Cu and CdTe powders.@footnote 1@ Micro Raman experiments carried out on the Cu powder particles showed the existence of a CuO overlayer. However, the presence of such oxide, or of oxygen molecules, have not been detected as important components in the films. The role that oxygen plays during the growth and properties of the Cu@sub x@Cd@sub 1-x@Te films is unknown to date. In this work we report the results of a study about the effects of incorporating controlled amounts of oxygen during the growth of Cu@sub x@Cd@sub 1-x@Te thin films, on their crystalline structure, composition, and optical and transport properties. This study was carried out in a two-target sputtering system, in which one target is made of Cu and the other of CdTe. The native oxide on the Cu target surface was removed previously by presputtering for a few minutes before opening the deposition shutters. The controlled incorporation of oxygen into the chamber was achieved by using an electronic mass flow controller and the elemental composition profiles obtained by Auger spectroscopy. @FootnoteText@ @footnote 1@J. Vac. Sci. Technol. A 17, 1958 (1999); Thin Solid Films 342, 1 (1999); Microelectronics Journal 31, 429 (2000).

TF-ThP6 Reactive Dual Magnetron Sputtering Technology for Oxide Dielectric Film Deposition*, S. Xu,* HIVAC Technology(GROUP) CO. LTD, P.R. China*; X. Hou,* Tsinghua University, P.R. China*; C. Fan,* HIVAC Technology(GROUP) CO. LTD, P.R. China*; L. Zhao, L. Cha,* Tsinghua University, P.R. China

A study on oxide dielectric film deposition by medium frequency (MF) reactive dual magnetron sputtering (DMS) is reported in this paper. A continuous system for large-area deposition by DMS has been developed more than two years ago. The operation state of the DMS depends on the hysteresis curve of the target voltage with respect to the reactive gas (O@sub 2@) flow rate. The process was controlled by adjusting O@sub 2@ flow based on the target voltage in the closed-loop. Possible mechanism of physical and chemical processes on the target/substrate surface has been discussed. Based on the detailed experimental studies, criteria of the operation point according to the hysteresis were summarized. It was shown that magnetic field profile, distance between the two targets, structure of the shield, arrangement of the pipes for reactive gas supply and direction of the O@sub 2@ flow have strong influence on the time constant and film quality as well as the precision and stability of the feedback closed-loop. Characteristics of deposited SiO@sub 2@, Al@sub 2@O@sub 3@ and TiO@sub 2@ films have been evaluated, including thickness, uniformity, surface topography, crystal structure, stoichiometric composition, refractive index and transmittance, etc. Long term operation confirmed that uniform, dense and amorphous optical film could be deposited rapidly and stably.

TF-ThP7 Copper Metallization for ULSI Using 90°-bend Magnetic Filtered Cathodic Arc Evaporation Plasma System*, J.-H. Lin,* National Tsing Hua University, Taiwan, Taiwan, ROC*; U.-S. Chen, W.-J. Hsieh, H.C. Shih,* National Tsing Hua University, Taiwan

The cathodic arc evaporation plasma generated the highest plasma density compared with other PVD systems, but is known to be contaminated with macroparticles. In order to produce high quality defect-free copper films, a 90X-bend magnetic filter is suitable for ULSI interconnects metallization application. Macroparticle contamination has been alleviated by magnetic filter, the copper ions in the fully ionized copper plasma were accelerated and deposited on the wafer with a negative pulsed bias voltage. The fully ionized copper plasma flux was highly directionally deposited on the patterned and blank wafers, the filling of trenches/vias as narrow as 0.2 µm, with an aspect ratio as high as 7, FESEM and TEM images showed conformable copper step coverage ability. Both XRD and SEM/EBSD spectra showed that the FCAE-deposited copper film has an obvious Cu(111) preferred orientation. The result of this process as made, by scratch tests, showed that higher substrate bias and 50% pulse bias duty cycle can effectively enhance the adhesion strength of copper film on TaN layer.

TF-ThP8 Velocities and Ionization Degree of Vapor Stream Produced from Evaporation Source using Porous Rod by Electron Beam Heating*, H.M. Ohba,* Japan Atomic Energy Research Institute, Japan*; T. Shibata,* Japan Atomic Energy Research Institute

A metal vapor was produced by electron beam heating with high thermal efficiency using a hearth liner and a porous rod for copper and cerium. While the top surface of the porous rod was heated by electron beam, the molten evaporation material surrounding the rod was transferred to the top surface by capillarity; then the atomic vapor stream was produced from the top surface. The ionization degree and the vapor velocities were measured with Langmuir probes, and a microbalance or laser induced fluorescence. The vapor characteristics were compared by evaporation from the bare water-cooled copper crucible. The ionization degree in the metal vapor is proportional to the electron beam current of the electron gun. In the case of evaporation from the porous rod, so a large amount of vapor flux can be produced at low electron beam current that the degree of ionization of metal vapor in the vicinity of the source is very low. The velocities of vapor produced from the porous rod were lower than that from the bare crucib le even at high vapor flux. The lower velocity for the porous rod was explained as follows. The excitation and ionization energies of the atoms evaporated by electron impact are converted to the kinetic energy of the vapor atoms by atom-atom collision. In the case of the porous rod, the rate of electron impact ionization of the evaporated atoms is lower than that of the bare crucible.

TF-ThP9 Effects of Plasma Exposure on Structural and Optical Properties of TiO@sub2@ Films Deposited by Facing Targets Sputtering*, T. Takahashi,* *H. Nakabayashi, N. Sasai, K. Masugata,* Toyama University, Japan

In sputtered films, it is very important to investigate the influence of plasma exposure to the substrate because the properties of films strongly depend on the plasma state. So, in this study, TiO@sub2@ films have been deposited at different substrate positions using the facing targets sputtering which can easily vary the degree of plasma exposure. The plasma was confined sufficiently between two Ti targets faced each other. The substrates were placed at a certain distance from the middle of a straight line connecting the centers of the targets' planes. TiO@sub2@ films with thickness of about 2-3 µm were reactively deposited on glass-slide substrates. The crystal structure, and optical properties of films were measured using a X-ray diffractometry and a Raman spectroscopy, and a spectrophotometer, respectively. The A(101), A(200), A(112) and A(220) peaks were observed from the X-ray diffraction patterns, where A shows an anatase of TiO@sub2@. With increasing plasma exposure, X-ray peak intensities I@subP@ of A(101) and A(200) gradually decreased, and I@subP@ of A(112) and A(220) gradually increased, respectively. I@subP@ significantly depended on the substrate position in this study. Moreover, A(220) peak was significantly higher than others and the TiO@sub2@ crystallites became larger with an increase of plasma exposure. TiO@sub2@ films also showed anatase from the Raman spectra with Raman shift of 145 cm@super-1@. With decreasing plasma exposure, the changes in the optical transmittance spectra of TiO@sub2@ films were very small at the wavelength of 350-900 nm. However, the transmittance spectra significantly depended on the wavelength with increasing plasma exposure. The transmittance monotonically decreased with decreasing wavelength in the range of 700 to 350 nm. Consequently, it was found that crystal structure and optical properties of TiO@sub2@ films were strongly affected to plasma exposure during deposition.

TF-ThP10 High Rate Deposition of TiO@sub 2@, TiN, and TiO@sub 2@/TiN/TiO@sub 2@ Thin Films Using New High Power Magnetron Sputtering Source and Comparison with Its Optical Characteristics*, M.J. Jung, H.Y. Lee,* ***Y.-S. Sin****, J.G. Han, J.-H. Boo,* Sungkyunkwan University, Korea

Thin films of TiO@sub 2@, TiN and TiO@sub 2@/TiN/TiO@sub 2@ were deposited on glass substrates at a temperature below 200 °C using a newly developed pulsed DC magnetron sputtering source with high power (20 - 150 W/cm @super 2@) and unbalanced magnetron. Titanium metal target (4-inch diameter, 99.9% purity) was mounted onto the sputtering sources, and oxygen and nitrogen were used as reactive gases and argon as working gas. Highly oriented, crack-free, stoichiometric polycrystalline TiO@sub 2@(101) and TiN(100) thin films were successfully grown on glass surfaces at 200 °C. In the case of the TiO@sub 2@ deposition, a thin film with high transmittance (90%) in the visible range was obtained while the TiN films showed very high reflectance (70%) in the infrared region. In this study, however, we found that the transmittance and reflectance are strongly influenced by the film thickness and the film surface roughness. For comparison, a multilayer film of TiO@sub 2@/TiN/TiO@sub 2@ was also deposited on glass substrates under the same growth condition as for TiO@sub 2@ and TiN thin films based on computer simulation results. Quite good optical properties can be obtained for the as-grown multilayer films. The most excellent values of transmittance (85%) and reflectance (80%) were found for a thin film with TiO@sub 2@ (380 nm)/TiN (20 nm) /TiO@sub 2@ (440 nm)/glass structure. The high IR reflection indicates that the as-grown multilayer film can be applied for heat mirrors.

TF-ThP11 Deposition of Dielectric Films by Photo Chemical Vapor Deposition using Vacuum Ultraviolet Xe2 Excimer Lamp from Tetraethoxysilane*,* ***N. Horii****, A. Inouye, H. Nishibata,* Fukui National College of Technology, Japan*; K. Okimura,* Tokai University, Japan

Dielectric films have deposited by photo-chemical vapor deposition (CVD) using Xe2 excimer lamp as a vacuum ultraviolet light source. Tetraethoxysilane was used as a silicon source. The goal of the research was to obtain insulation films for between layers in LSI fabrication and plasma free environment for sensitive substrate at low temperature. First, photo-chemical dissociation process of TEOS in the gas phase was investigated by in-situ mass spectrometry. We have found that TEOS was dissociated by VUV irradiation while releasing alkyl groups such as CxHy (x=1-2,y=2-5). Moreover, almost all Si-O bonds of TEOS were not broken at the energy of Xe2 excimer light. These are main reaction of the forming precursors for film deposition in the photo CVD process. A structure of films was investigated by FTIR analysis. The film prepared from TEOS at room temperature was SiOxCx like film having large amount of CH groups, however, Si-OH bonds was not included. Investigation of a stability of the films in ambient air was obtained undesirable results such as the Si-OH bonds increased and the film thickness decreased by the day. In order to improve a stability of the films we have irradiated VUV light to deposited films at room temperature. The result from the technique was effective for reducing unstable CH groups contained in the films and obtaining a good chemical and physical stability.

TF-ThP12 Bahaviours of Energetic Oxygen Particles in the Reactive Sputtering of Zr Target in Oxygen Atmosphere*,* ***K. Tominaga****, T. Kikuma, K. Kusaka, T. Hanabusa,* The University of Tokushima, Japan

ZrO@sub@2 films were deposited in oxygen atmosphere with conventional planar magnetron sputtering system. In a sputtering of oxide target, energetic negative oxygen ions and energetic neutral oxygen atoms are bombarding the film. Then energetic oxygen ion s are generated in cathodefall in front of an oxide target. Precauser of the energetic neutral atoms is the negative oxygen ions that are accelerated in the cathode fall. These energetic particles bombard depositing oxide film and degrade film qualities s uch as internal stress, insulative characteristics. However, these energetic particles in a reactive sputtering is not so clear, especially in cases of materials such as Zr that is active with oxygen. We investigated the degree of the energetic oxygen particles in ZrO@sub2@ deposition and the generation mechanism of the energetic oxygen particles. Strong energetic oxygen ions generated in the sputtering of the Zr oxide target in O@sub2@ atmosphere were ascribed to the strong oxidization at the Zr surface. The energetic negative oxygen ions were detected using a probe constructed here. At the same time, the photoemission intensity from the sputtered Zr atoms was observed in order to monitor the target surface oxidization. The results show that the Zr targe t is very active with the oxidization of the target surface and drastically oxidized in a metal mode sputtering. The strong negative oxygen ions in an oxide mode sputtering are due to the generation of thick Zr-oxide layer on the Zr target. At the same time, films were prepared by the two sputtering modes and the relation the film properties and the energetic oxygen ions were investigated.

TF-ThP13 In-situ Fabrication of Polycrystalline Thin Film Cathodes for Secondary Thin Film Batteries using Radio Frequency Sputter Deposition*, K.-F. Chiu,* ***F.C. Hsu****, M.K. Wu, T.-P. Perng,* National Tsing Hua University, Taiwan

In situ deposition of polycrystalline LiNi0.8Co0.2O2 thin films was performed using radio frequency magnetron sputter deposition on indium tin oxide substrates. Different substrate temperatures, upto 500 oC, were applied during deposition. The films deposited at elevated temperature exhibited a strong preferred orientation (or texture). It was found that varying the substrate temperature resulted in changing in film texturing. As the substrate temperature increased, the film structure changed from non-crystalline to polycrystalline with enhanced preferred orientation. The film texture was examined using X-ray diffraction (XRD) method. The surface morphology was observed using optical microscope and scanning electron microscope. The compositions of the targets and films were characterized by an inductively coupled plasma spectroscopy method (ICP) and were found to be identical. The change of texturing was interpreted by volume strain energy and surface energy minimization. Textured polycrystalline thin films can be deposited by controlling the deposition temperature. The technique was also used to deposit polycrystalline LiCoO2, LiNiO2 and LiMn2O4 thin films, and similar results were obtained.

TF-ThP14 Effects of Deposition Parameters and Physical Properties of Thin NiO Films on Gas Sensing Characteristics*,* ***I. Hotovy****,* Slovak University of Technology Bratislava, Slovakia*; L. Spiess,* Technical University of Ilmenau, Germany*; P. Siciliano, S. Capone,* IME-CNR Lecce, Italy

Our research has been focused on the preparation and characterization of NiO thin films deposited by reactive magnetron sputtering. Small gas sensors on alumina substrate with different NiO thin films were fabricated and then were investigated their physical and sensing properties for application to nitrogen oxide. In order to apply NiO thin films to the nitrogen oxide gas sensor, NiO thin films (2000 Å) were prepared by dc reactive magnetron sputtering from a nickel metal target in an Ar@+@ O@sub 2@ mixed atmosphere in two sputtering modes. Details about the deposition of NiO have been reported in previous papers.@footnote 1@ The oxygen content in the gas mixture varied from 20 to 60 %. The films deposited in the metal-sputtering mode resulted in a polycrystalline (fcc) NiO phase with nearly stoichiometric composition. On the contrary, the films prepared in the oxide-sputtering mode were amorphous and oxygen rich. The post-annealing (500@degreeo@C) of as-deposited NiO thin films changes amorphous to the (fcc) NiO phase for samples prepared in oxide-sputtering mode. TEM observations revealed a dense fine-grained structure with the grain size in the range 40-100 Å. AFM showed that the surface morphology NiO films could be modified by the process parameters as the oxygen content and the pumping speed. SEM observation and EDX analyses revealed uniform morphology and homogenous dispersion of NiO, Pt and Al@sub 2@O@sub 3@ phases. We have investigated the sensitivity (I@sub g@/I@sub o@) versus operating temperature of NiO films when a concentration varied from 1 to 10 ppm of NO@sub 2@. @FootnoteText@ @footnote 1@ Hotovy, I., Huran, J., Spiess, L., Hascik, S.: Sensors and Actuators B 57 (1999) 147-152.

TF-ThP16 Computer Modeling of Thin Metal Films for Advanced Devices*,* ***L He****,* San Jose State University

Computer simulation for semiconductor devices and process is becoming more and more important due to the high cost of device fabrication and processing. In recent years, semiconductor optoelectronic device has undergone explosive growth. This growth has fueled a vast expansion of device modeling and simulation. Low temperature (LT) process on metal thin film has been proven effective to increase Schottky barrier height and reduce film resistivity in recent study. For the potential application of LT process in advanced semiconductor devices, a computer simulation program is developed. The computer simulation focus on microstructure and electric properties of the thin metal films. Metal-semiconductor-metal (MSM) photodetectors are widely used in the optoelectronic integrated circuit receivers because of their compatibility with the preamplifier for their planar integration scheme, the minimum number of processing steps, high performance, and low cost. InGaAs/InP is chosen for long wavelength application. In this work, analysis based on the results of computer simulation is presented. The Ag/InGaAs/InP contact formed by LT process showed that the Schottky barrier height is as high as 0.64eV. This value is more than double of the barrier height when processed in room temperature. It is believed that the LT process could greatly enhance the performance of a MSM photodetector. The device simulation includes RC time simulation, frequency response, and efficiency analysis.

TF-ThP18 Structural Stability of Amorphous Al78W22 Thin Films Below Crystallization Temperature*, **N. Radic,*** Rudjer Boskovic Institute, Croatia*; J. Ivkov,* Institute of Physics, Croatia*; A. Tonejc,* Faculty of Sciences, Croatia*; T. Car,* Rudjer Boskovic Institute, Croatia

In this work the structural stability of Al78W22 amorphous thin films upon isochronal and isothermal heating below crystallization temperature (about 840 K) is reported. The amorphous Al78W22 films were prepared by a magnetron co-deposition onto alumina ceramic, sapphire, and glass substrates, held at four temperatures: LN2, RT, 200 degC, and 400 degC, respectively. Their stability was investigated by a continuous in situ electric resistance measurements during a two kinds of thermal treatment: a) A cycle of isochronous heating of the as-deposited sample up to 790 K, isothermal annealing at that temperature for 6 hrs, followed by cooling to room temperature. A strong irreversible variation of the film electrical resistivity is observed upon first heating. It is less pronounced at higher heating rates, presumably due to the competition between the relaxation of amorphous structure and temperature dependence of the resistivity. Deposition onto substrates held at high temperatures also strongly reduces the amount of resistivity variation. b) Isothermal annealing at high subcrystallization temperatures (803, 813, and 823 K) for several tens of hours resulted in a partial phase transformation of the amorphous alloy into the intermetallic Al4W compound. The Johnson-Mehl-Avrami model analysis of the phase transformation kinetics yields the Avrami coefficent close to 1, suggesting a nucleation as a crystallization mechanism. The above results show that the amorphous Al78W22 films require an initial annealing in order to attain the structural stability against heating, which is then retained in a marked degree even during a prolonged heating at the high subcrystallization temperatures.

TF-ThP19 Composite Ti/C:H Films and Their Potential Application*, H. Biederman, D. Slavinska, H. Boldyreva, S. Gretchany,* Charles University, Czech Republic*; **S. Kvasnica,*** Boltzmann Inst. for Biomedical Microtechnology and Vienna Univ. of Tech., Austria*; W. Fallmann,* Vienna University of Technology, Austria*; L. Bacakova, V. Stary,* Academy of Sciences of the Czech Republic

Titanium containing carbonaceous thin films have been examined for some time because of their tribological properties@footnote 1-4@ and because of the prospect of their biomedical applications.@footnote 5,6@ Composite Ti/CH films reveal hardness Hv up to 35 GPa and coeficient of friction below 0.3 for Ti concentrations below 40 at % The presence of Ti in C:H matrix causes cellular reactions of bone marrow cells. Therefore Ti/C:H hard coating can be applied for bone implants. Composite Ti/CH films were deposited using an unbalanced dc planar magnetron equiped with Ti target operating in Ar/n-hexane or Ar/methane mixtures. Deposition process is described in relation to composition and structure as well as basic electrical, optical properties and hardness of the films. XPS analysis of the film surface revealed considerable oxidation and static contact angle of a water droplet ranged from 68 to 85 deg. The potential application of these films for bone implants has been assessed. @FootnoteText@ @footnote 1@ N.E. LoBiondo, R. R. Aharonov, R. P. Fontana, Surface and Coatings Technol.,94-95(1997), 652-657 @footnote 2@ C. Donnet, J. Fontaine, T. LeMogne, M. Belin, C. Heau, J.P. Terrat, F. Vaux, G. Pont, Surface and Coatings Technol.,120-121(1999), 548-554 @footnote 3@ T. Krumpiegel, H. Meerkamm, W. Fruth, C. Schaufler, G. Erkens, H. BÃ¶hner, Surface and Coatings Technol.,120-121(1999), 555-560 @footnote 4@ T. Zehnder, J. Ptscheider, Surface and Coatings Technol.,133-134(2000), 138-144 @footnote 5@ R. Hauert, L. Knoblauch-Mayer, G. Francz, A. Schroeder, E. Wintermantel, Surface and Coatings Technol.,120-121(1999), 291-296 @footnote 6@ L. Bacakova, V. Stary, O. Kofronova, V. Lisa: Polishing and coating carbon fibre-reinforced carbon composites with a carbon-titanium layer enhances adhesion and growth of osteoblast-like MG63 cells and vascular smooth muscle cells in vitro, J. Biomed. Mater. Res. in press 2001.

TF-ThP20 The Effect of Substrate Bias and Nitrogen Incorporation on the Diamond-like Carbon Film Depositions by 90°-bend Magnetic Filtered Cathodic Arc Evaporation Plasma*, **W.-J. Hsieh,*** National Tsing Hua University, Taiwan*; J.-H. Lin,* National Tsing Hua University, Taiwan, Taiwan, ROC*; P.-S. Shih, X.-W. Liu, H.C. Shih,* National Tsing Hua University, Taiwan

The properties of nitrogen incorporated diamond-like carbon (DLC) films were deposited on silicon (111) wafers by a 90°-bend Magnetic filtered cathodic Arc Evaporation Plasma system. The structure and properties have been studied by TEM/EELS, Raman spectra, Vickers hardness, RBS, and SIMS spectra. For the DLC depositions using highly ionized energetic plasma, carbon ions with varying energies can form different types of carbon bonding in the films. The energies can be controlled by applying a variable bias to the substrate. It has been reported that the DLC films have the highest hardness with a substrate pulsed bias between -100V to -150V, and the maximum sp@super3@ bonding content can be obtained at a pulsed bias of -150V (duty cycle:50%) is up to 85% as measured by TEM/EELS. The DLC films have a higher hardness when the content of sp@super3@ bonds have a higher fraction of sp@super3@ bonding contents. The hardness seems to be related to the Raman I(D)/I(G) ratio. It also founds that nitrogen content increases with increasing substrate bias and the deposition temperature on DLC films. However, the deposition above 400°C causes a sudden loss of sp@super3@ bonding. The maximum incorporation of nitrogen to the DLC films was measured up to 15%(N) by SIMS as well as RBS.

TF-ThP21 DLC Thin Films Characterized by AES, XPS and EELS*, **E.C. Samano**, G. Soto, L. Cota,* CCMC-UNAM, Mexico

DLC films have been grown by laser ablating a graphite target in a UHV system. Two kinds of depositions are processed depending on the experimental conditions, a HOPG film and a DLC film. A relationship of the film microstructure with laser power density and substrate conditions was observed. The films are in situ monitored and characterized during the first stages of the deposition process by means of surface spectroscopic techniques, such as AES, XPS and EELS. The film microstructure is confirmed by SEM. Clear evidence of a SiC interface of two monolayers thick was clearly observed to form due to the reaction of the first carbon species impinging on the substrate surface.

TF-ThP22 Physical Properties of Nitrogen Doped Diamond-Like Amorphous Carbon Films Deposited by Supermagnetron Plasma CVD*, **H. Kinoshita**, N. Otaka,* Shizuoka University, Japan

Diamond-like amorphous carbon films doped with nitrogen (DAC:N) were formed using a supermagnetron plasma chemical vapor deposition (CVD) method.@footnote 1@ The electrical conductive DAC:N films were studied for the fabrication of high performance field emitters. DAC:N films were deposited on Si and glass wafers intermittently using i-C@sub 4@H@sub 10@/N@sub 2@ repetitive plasma CVD. CVD duration was selected to be 40sec or 60sec, and several layers were deposited repetitively to form one film. Physical properties such as deposition rate, hardness, resistivity and optical band gap were measured at lower-electrode temperature of 100 °C as a function of upper- and lower-electrode rf powers (200W/200W-1kW/1kW) and N@sub 2@ concentration (0-80%). With increase of rf powers supplied to two electrodes, resistivity, hardness and optical band gap decreased monotonously. Refractive index, however, was almost constant to 2.0-2.1. With increase of N@sub 2@ concentration at rf powers of 1kW/1kW, deposition rate, hardness, resistivity and optical band gap decreased monotonously. With increase of plasma CVD duration from 40sec to 60sec, resistivity decreased to 0.032@ohm@cm and optical band gap decreased to 0.02eV, at N@sub 2@ concentration of 80%. FT-IR spectroscopy measurements revealed that, with increase of N@sub 2@ concentration, absorption peak intensities of NH single and CN triple bonds increased and that of CH single bond decreased. @FootnoteText@@footnote 1@H.Kinoshita and M.Yoshida, J.Vac.Sci.Tecnol.A 19, July (2001).

TF-ThP23 Fabrication of Diamond Photocathode of Transmissive Type*, **K. Kato**, K. Ito, M. Hiramatsu, M. Nawata,* Meijo University, Japan*; C.H. Lau, A. Bennett, J. Foord,* University of Oxford, UK*; R. Jackman,* University College London, UK

Diamond is attractive as a "visible-blind" photocathode material for UV imaging, in view of its wide band gap and optical absorption properties, electrical transport characteristics and chemical stability. Under the negative electron affinity (NEA) condition, when the photon energy is higher than the band gap, the electrons are excited to the conduction band as a result of UV absorption, transported to the surface and then escape into vacuum. In order to realise the efficient diamond photocathode, it is n ecessary to optimise the optical absorption coefficient, the electron diffusion length in the bulk, and the surface escape probability. An investigation of these parameters is the purpose of the current work. Two types of diamond photocathode have been fabricated, for conventional reflective mode (UV photons and electrons interact with the same surface) and, for the first time, the more demanding trasnsmissive mode operation (electrons emitted from the opposite surface to the incoming UV light). The efficiencies of these two designs are compared and discussed in terms of the fundamental optical and electronic properties of the diamond films. In addition, we have investigated systematically the influence of a variety of surface treatments upon the photo-emissive properties of diamond photocathode, with differing levels of hydrogenation and oxidation. As a result of oxygen surface treatment, a drastic decrease in the photocurrent was observed. The use of the alkali metals, caesium and potassium in conjunction with various oxidation treatments is therefore explored in order to stabilise high quantum photo yield.

TF-ThP24 Fabrication of Carbon Whisker Film Using RF Plasma CVD*, **K. Ito**, K. Kato, M. Hiramatsu, M. Nawata,* Meijo University, Japan*; M. Hori,* Nagoya University, Japan*; C.H. Lau, J. Foord,* University of Oxford, UK

In the case of film formation by utilizing the plasma enhanced chemical vapor deposition (PECVD) method, it is desirable to supply selectively reactive species suitable for the film growth onto the substrate. Previously we demonstrated the successful formation of diamond crystals using a unique PECVD system, which has the parallel-plate capacitively coupled radio-frequency (rf, 13.56 MHz) discharge plasma assisted by the hydrogen radical source using the remote microwave (2.45 GHz) discharge plasma.@footnote 1@ In the present work, by using this system with a mixture of C@sub 2@F@sub 6@ and H@sub 2@, carbon films with whisker array were successfully formed on Si (100) substrate at C@sub 2@F@sub 6@/H@sub 2@=0.3/13 Pa, rf power of 100W, microwave power of 100W, and substrate temperature of 600 °C. Deposited films were characterized by scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. Although fluorocarbon gas was used as a source gas, fluorine was not detected in the deposited film from the XPS analysis. Surface morphology was changed from pyramids to whiskers according to the deposition conditions. Field emission characteristics have been investigated for the fabricated carbon film with whisker array. The V-I characteristics revealed a current density of 750 µmA/cm@super 2@ at an applied field of 60 V/µmm. Corresponding Fowler-Nordheim plot was well fitted by the straight line, indicating that the field emission property can be explained by a tunneling mechanism. @FootnoteText@ @footnote 1@M. Hiramatsu, M. Inayoshi, K. Yamada, E. Mizuno, M. Nawata, M. Ikeda, M. Hori, T. Goto, Rev. Sci. Instrum., 67 (1996) 2360.

TF-ThP26 Effect of Ar Addition on Microstructure and Composition of Nitrogen Containing Carbon Films Prepared by Hot Filament CVD*, **Y. Watanabe**, A. Yamazaki, N. Kitazawa, Y. Nakamura,* National Defense Academy, Japan

Nitrogen containing amorphous carbon (a-CNx) films were synthesized on Si (100) substrates by hot filament chemical vapor deposition method using a carbon filament, which supplies carbon and heat. Deposition was performed in low pressure atmosphere of pure nitrogen and a gas mixture of nitrogen and argon. Effects of argon addition on film microstructures and composition were studied by changing the argon fraction under the total pressure of 100 Pa. The film microstructure was observed by field-emission scanning electron microscope (FE-SEM) and the composition was analyzed by X-ray photoelectron spectroscopy (XPS). FE-SEM observations reveal that films prepared in pure nitrogen atmosphere show a columnar structure, while the films change to tapered structure with argon addition. Spectra of XPS show that the films were composed of carbon and nitrogen, and no contamination was observed except a small amount of oxygen. It is also found that the nitrogen concentration in films increases in dependence on argon partial pressure.

Vacuum Science & Technology
Room 134/135 - Session VST1-ThP

Pressure Measurement & Calibration Poster Session

VST1-ThP1 A Constant Volume Flowmeter for Calibrating Mass Flow Meters*, D. Tian,* Lanzhou Institute of Physics, P.R. China, P.R.China*; **X. Wen**,* Lanzhou Institute of Physics, P.R. China

The mass flow meters are used almost exclusively in the semiconductor industry for the admission of process gases. While they have been used in the semiconductor industry for over twenty years, their performance still remains to be understood about gas factor, orientation, pressure, and temperature effects. Therefore, the mass flow meters need to be calibrated so as to reduce the systematic errors and improve their interchangeability and reliability. In order to calibrate the mass flow meters, a constant volume flowmeter was made in Lanzhou Institute of Physics (LIP). The principle of the flowmeter is to measure pressure change rate with constant volume. The flow is the product of volume and pressure change rate. The vacuum system is all made of metal. The calibration chamber, whose inner surface is treated by electric-chemical polishing, is cylinder-shaped with stainless steel. Rotary pump, which is used to evacuate the chamber, is the main pump of this system. The gravimetric and gas expansion methods are used to measure the chamber volume precisely. The pressure, time interval, and temperature are measured by a high accurate capacitance diaphragm gauge (CDG), a quartz oscillator and a platinum resistance thermometer, respectively. The apparatus is controlled by computer to fulfill the automatic operation and avoid the effect from operators. Constant volume method is a powerful method for calibrating the mass flow meters. There are many disturbing factors in this method, such as change of temperature, adsorption, outgassing, leak, etc. These factors are considered during the design of this apparatus and confined to reasonable scope. The range of the flowmeter is 10@super -3@~100 Pam@super 3@/s (1 sccm~50 slm) with uncertainty less than 1.2%. The main sources of uncertainty are pressure measurement and the temperature change. The uncertainty can be lowered by making a study of the CDG's property and decreasing the vibration of temperature.

VST1-ThP3 Calibration Apparatus of Mass Spectrometer for Partial Pressure Analysis using Dynamic Flow Method*, D. Li, Z. Li,* LanZhou Institute of Physics, P.R. China*; **F. Yan**,* LanZhou Institute of Physics, P.R. China, China*; D. Zhang, J. Zhang, H. Xu, Y. Gong, L. Li,* LanZhou Institute of Physics, P.R. China

In order to solve the problem of calibration of mass spectrometer, we had designed and made the calibration apparatus of mass spectrometer for partial pressure analysis using dynamic flow method, which had the ability to calibrate all kinds of mass spectrometer. The calibration apparatus was composed of the source system of gas, the inlet system of gas, the chamber of calibration, the pumping system, the collecting and processing system of data. To gain the accurate measure of partial pressure,we adopted spin rotary gauge(SRG) as the measure standard.the measurement range is 10 @super -1@ to 10@super -6@Pa. There were three independent source and inlet systems of gas in the same structure in the calibration apparatus. Gas brought from anyone of three independent source and inlet systems of gas can produce a partial pressure ranged from 10@super -1@to 10@super -6@Pa. Thus, it not only provides the basic for calibrating, but also is easier to calibrate. To acquire the well-distributed molecular flow in the chamber of calibrating, the spherical chamber of calibrating is 350mm in diameter. On the basic symmetry principle, the normal of the equator plane on which seven CF35 and a CF63 were mounted on the spherical chamber was aligned with the boresights of the inlet aperture and the outlet aperture to the chamber, so that SRG and calibrated mass spectrometer located in the same condition. To realize automatic collecting and processing of data, we have applied the computer technology .the software designed on our own is convenient for user. the main technical data is: Ultimate pressure: 5Ã—10@super -7@Pa Calibration range: 10@super -1@ to 10@super -6@Pa uncertainty: @<=@4.8% Calibrated gas: 1 to 3 different gas The calibration apparatus can be used for calibration of sensitive,linearity,stability ,etc of mass spectrometer.

VST1-ThP4 The Role of Viscosity Parameter in the Calibration of a Spinning Rotor Gauge*, **P. Mohan**,* National Physical Laboratory, (NPL), India

Spinning rotor gauges (SRGs) act as transfer standards for measurement of pressures in the range 1 Pa to 10@super-4@ Pa. There are two methods for the measurement of the gauge calibration factor. In the first, the gauge is connected on a primary standard and pressures in the range 0.1 to 1 Pa are generated and the viscosity parameter is entered as equal to zero in the gauge controller. Then a plot of the ratio of indicated pressure to the real pressure (=@sigma@@subeff@) against the real pressure is obtained as a line with negative slope. The intercept of this plot for the real pressure equal to zero gives the gauge coefficient. In the second method, the same procedure is adopted but the actual value of the viscosity of the test gas is entered into the controller. The plot obtained in this case is a horizontal line. The average of the different @sigma@@subeff@ values gives the gauge coefficient. This paper gives the results obtained at the National Physical Laboratory (N. Delhi)for the calibration of three SRGs by the two methods and shows that agreement of ±0.1 % is obtained in all the three cases.The real pressures were generated using the NPL primary standard based on the principle of static expansion.

VST1-ThP5 Primary and Secondary Vacuum Standards Based on Piston-cylinder Technique*, **J. Tesar**, D. Prazak,* Czech Metrology Institute, Czech Republic

In the last years there were developed vacuum standards based on the piston principle with several construction designs. They can be utilised both in primary and in secondary metrology of vacuum. Covered ranges start at atmospheric pressure and reach the tenths of pascal. The attainable accuracy of top standards is fully comparable with other physical principles (mercury columns, static expansion, CDG). The first part of this paper will briefly summarize the most important construction designs, including ranges and attainable uncertainties. The second part of presentation will describe basic primary methods of calculation of effective area from dimensional measurement for classical, non-rotating, divider and conical design of primary piston standards of vacuum. In the third part the basic methods of secondary traceability will be shown: direct comparison with a liquid column standard, direct comparison with a static expansion system and three types of cross-floating comparisons in absolute pressure mode. Description of every method will be supplemented by a typical example from CMI praxis including full uncertainty budget.

VST1-ThP6 Clamshell Leak Testing Tools*, J.C. Brunet,* CERN-now retired, Switzerland*; P. Coly, **P. Cruikshank**, M. Duret, M. Genet, A. Jacquemod, N. Kos, H. Nemoz,* CERN, Switzerland*; P. Trabujo,* SGS Qualitest, France

The Large Hadron Collider (LHC) is the next accelerator being constructed at CERN. Over 40000 in-situ welds will be performed on the helium and vacuum systems in the LHC tunnel. Elastomer clamshell tools have been developed to permit high sensitivity leak testing of welded tubular connections using the so-called "hood" technique. The application, design and peformance of the clamshell tool will be described.

VST1-ThP7 Pressure Leak Calibration Apparatus*, **D. Zhang**,* Chinese Vacuum Metrology Center, P.R. China

Pressure Leak Calibration Apparatus is a metrology standard for calibrating gas leak rate and has been used to calibrate the pressure leak. Pressure leak is a kind of instrument, on the condition of defined temperature and inlet pressure (more than one atmosphere), to offer known leak rate to one atmosphere side. The pressure leak apparatus is composed of the system of constant volume method and the system of dynamic comparison method with quantitative gas. In the constant volume method, the pressure of constant volume is measured by absolute pressure method and differential pressure method, which both expends the lower limit and upper limit of measurement. In the dynamic comparison method with quantitative gas, the problem of verifying the unknown trace gas is solved with quantitative method. The sample of mixed gas and quantitative gas are produced with pressure reduction method and the gas introduced respectively into mass spectrum chamber with molecular flow method is analyzed by mass spectrum. With such technique, the repeatability is guaranteed. And the lower limit is expended for 2 orders and the small leak rate accordingly can be calibrated. The pressure leak can be calibrated with these two methods, respectively. In the multiple range of both the constant volume method and the dynamic comparison method with quantitative gas, there is satisfactory agreement. The range of constant volume method is from 1¡Á10@super 2@to 5¡Á10@super-3@PaL/s, uncertainty is from 2.6% to 9.1%£»the range of dynamic comparison method with quantitative gas is from 2¡Á10@super-2@ to 5¡Á10@super-5@Pa L/s, uncertainty less than 14.2%.

VST1-ThP8 The Study of Leak Detection for Multi-systems with Mass Spectrometer*, **Y. Rongxin**,* BeiJing Spacecraft, P.R.C

The apparatus of leak detection for multi-systems with mass spectrometer is consisted of the leak detection cumulating vessel, sampling cycle system, beginning gas cumulating vessel, pressuring gas equipment, leak rate calibration equipment. The multi-systems pressured different inert gas were put into the leak detection cumulating vessel and the leak detection cumulating vessel was sealed in the air environment. The gas in the leak detection cumulating vessel was pumped into the beginning gas cumulating vessel. After the multi-systems put into the leak detection cumulating vessel, the gas in the leak detection cumulating vessel was forced to uniform. The gas of the leak detection cumulating vessel and the beginning gas cumulating vessel was alternatively analyzed by the mass spectrometer and the ion currents was accordingly got. The calibrating gas was injected into the leak detection cumulating vessel. The gas of the leak detection cumulating vessel and the beginning gas was alternatively analyzed again. The leak rates of multi-systems were calculated. The search gas of different time in leak detection cumulating vessel was comparatively measured with beginning gas stored in the beginning gas cumulating vessel. Therefore, the problem of repeat and reliability of quadpole mass spectrometer in long time was avoided. The problem of quadpole mass spectrometer calibration was avoided by injecting the quantitative calibration search gas into the leak detection cumulating vessel. The ion current of calibration search gas and the ion current of end gas were the same level by controlling the quantity of injecting the quantitative calibration search gas. The problem of the linearity of quadpole mass spectrometer also was avoided.

VST1-ThP10 A Compact Leak Rate Calibration System*, **X. Chen**, Q. Zhang, Q. Liu, F. Yang, L. Cha,* Tsinghua University, P.R. China

A compact leak rate calibration system has been developed to meet the quality control of industrial leak detection, especially the growing needs of sniffing application. It was designed to calibrate the leak rate from high pressure to atmosphere (pressure leak), but can be used for vacuum leak (from atmosphere to vacuum) rate calibration also. A new method based on constant volume change in pressure for pressure leak rate calibration has been put forward. A differential capacitance diaphragm gauge (CDG) has been selected to decrease the temperature effect greatly. The system consists of a calibration unit and a computer. All of the data could be collected and processed automatically. A mechanical pump has to be added if the system is used for calibrating vacuum leak rate. The whole size of the calibration unit is 30 X 20 X 20 cm@super 3@ only. The main parts of the calibration unit are: 1. a reference chamber with a valve connected to atmosphere or a vacuum pump; 2. a calibration chamber with a valve connected with the calibrated leak; 3. a differential CDG; 4. an isolate valve between the above two chambers for pressure balance before calibration or turn on the test, the total valium of the reference region has been pre-calibrated and the calibration region including the outlet of the test leak can be calibrated by the system itself; 5. a temperature monitor unit; 6. an heat isolator system. It was proven that 1 X 10@super -5@ Pam@super 3@/s pressure leak rate at room temperature could be calibrated with an accuracy of better than ±5% (the confidential index is 95%) and the minimum pressure leak rate could be calibrated was 3 X 10@super -6@ Pam@super 3@/s with an accuracy of better than ±15% , when the environmental temperature change was within ±0.1°C. The total test period was about 30 minutes. The system is compact and suitable for leak rate calibration in industry.

Vacuum Science & Technology
Room 134/135 - Session VST2-ThP

Vacuum Issues in Accelerators Poster Session

VST2-ThP1 Vacuum System Design for the 3GeV-proton Synchrotoron of JAERI-KEK Joint Project*, **M. Kinsho**,* Japan Atomic Energy Research Institute, Japan

The 3 GeV synchrotron accelerator for JAERI-KEK joint project is aimed to supply a high-intensity proton beam to both the 50 GeV synchrotron ring and the neutron production target. For this purpose, the 3 GeV synchrotron, having a circumference of 313.5 m, is designed to accelerate a high-power beam of 1MW, by setting 25 Hz as a repetition rate and 8.3 x 1013 as a proton number for each acceleration. A rapid-cycling magnetic field is necessary to operate a synchrotron with such a high repetition rate. Since an eddy-current effect in a metal duct would produce an unacceptable perturbation of the magnetic field and unnecessarily large ohmic losses, an alumina ceramic is a candidate material for vacuum ducts in the dipole and quadrupole magnets. The required beam apertures, being a circular cross-section, are 187 and 247 mm in diameter for the vacuum ducts to be installed in the dipole and quadrupole magnets, respectively. The duct lengths for each magnet are 3.5 and 1 m. Since such a long duct is difficult to make with accuracy in the radial dimension, when sintered at once, it can only be manufactured by jointing duct segments of about 0.5 m long. The mechanical strength and deterioration under high level of radiation were examined for various kinds of alumina ceramic and for the joint. Almost all the ceramics to be tested have a sufficiently high flexural strength of 300 MPa, or more, before irradiating a 2.5 GeV-electron beam, and they did not show any significant deterioration in the flexural strength as far as an absorption dose is up to 1000 MGy.

VST2-ThP2 The Greatest Ultra-high Vacuum System of Cryopump in China*, C.Y. Zhang,* Beijing Institute of Satellite Environment Engineering, P.R. China*; **J.M. Chen,*** Beijing Institute of Satellite Environment Engineering, P.R. China, P.R. Cina

A large ultra-high vacuum facility of cryopump has been developed in China. The vacuum chamber in this facility consists of three parts, that is: the main chamber, 12m diameter and 22m height; the auxiliary chamber 7.5m diameter and 15m length; the special test chamber, 5m diameter and 15m length. The volume of the main and auxiliary chamber is 3200m@super 3@. The chambers are made up of the stainless steel. It is the greatest ultra-high vacuum facility in China. The roughing vacuum systems consist of 4 sets of the JZJLH-5000 roots vacuum pump system and a cold trap, which is 2m diameter and used as to prevent back streaming of pump oil. The roots vacuum pump system includes a ZJ-5000 main roots pump, a ZJB-1200 roots pump, a ZJL-600 circulatory gas cooled roots pump and a H150 rotary plunger vacuum pump. The degree of vacuum in the chamber can reach 0.7 Pa after 5h roughing time. The ultra-high pump systems in the main and auxiliary embrace the 8 sets of cryopump, which are installed on the outside of the chamber, an internal Helium cryopump (cryo panel), which is set in the chamber, and three sets of turbo molecular pump, which are used as auxiliary ultra-high pump system and the main pump for the vacuum leak system. The cryopump has a 5x10@super 4@l/S volume of flow rate, the internal Helium cryopump 2x10@super 6@l/S and the turbo molecular pump 2200 l/s. The vacuum measure system consists of the tens gauge heads and vacuum gauges, which include the nude gauge, Bayard-Alpert gauge, total pressure range of vacuum gauge. It can attain the measure range of pressure from 10@super 5@ Pa to 10@super -6@ Pa.

VST2-ThP5 Development of TiN Coating for the SNS Ring Vacuum Chambers@footnote *@*, P. He,* *H.C. Hseuh, R. Todd,* Brookhaven National Laboratory

The inner surface of the ring vacuum chambers of the US Spallation Neutron Source (SNS) will be coated with ~ 100 nm of titanium nitride (TiN). This will minimize the secondary electron yield from the chamber wall, and thus avoid the so-called e-p instability caused by electron multipacting as observed in positron storage rings and a few high-intensity proton storage rings. An R&D program has been carried out to develop coating parameters that give proper stoichiometry and suitable thickness for the vacuum chambers. DC sputtering and DC-magnetron sputtering were conducted in chambers of relevant material and geometry to SNS ring vacuum systems. Auger Electron Spectroscopy and Rutherford Back Scattering were used to analyze the coating for thickness, stoichiometry and impurity. Excellent results were obtained with magnetron sputtering. This paper will present the development of the coating process, the surface analysis results and the coating of the 4-m long production chambers. @FootnoteText@ @footnote *@Work performed under the auspices of the U.S. Department of Energy.

VST2-ThP6 DA@PHI@NE Vacuum Performance and Conditioning*, A. Clozza,*** Istituto Nazionale di Fisica Nucleare, Laboratori Nazionali di Frascati, Italy

A 510 MeV high luminosity @PHI@-factory is operating at INFN Frascati National Laboratory, Italy. The accelerator complex consists of a full energy Linac, a small damping ring and two electron-positron high current storage rings. The behaviour of the vacuum under operation, the dynamic pressure and the beam conditioning versus beam dose will be presented. A desorption efficiency below 1x10@super -6@ molec./phot. has been reached in some sections of the vacuum chamber, while a value in the range of some times 10@super -5@ molec./phot. has been reached in other sections. Possible reasons that could explain these differences will be also presented.

VST2-ThP7 Presentation of the ESRF Vacuum System from an Operational Point of View*, D. Schmied,*** European Synchrotron Radiation Facility, France

Since several years the European Synchrotron Radiation Facility [ESRF] serves 40 beamlines with a stable photon beam during 5600 h per year and a reliability of 97%. The vacuum system, as one of the subsystems, appears to pay an crucial role in the operation of such a facility. A review is given about the main difficulties experienced and the actions taken to overcome them. Aspects of instrumentation, interlocks, machine vacuum parts and control will be discussed.

VST2-ThP8 A White Irradiation Test facility at Elettra (WhITE)*, F. Mazzolini,*** *J. Miertusova, F. Pradal,* Sincrotrone Trieste S.C.p.A., Italy

Photon Stimulated Desorption (PSD) provides the primary gas load in Electron Accelerators and Storage Rings. Dedicated experimental setups have been installed in various Synchrotron Radiation Facilities in order to understand the vacuum behavior of different materials with respect to non monochromatized Synchrotron Light irradiation. This has been performed by measuring the variation of the desorption yield due to the accumulated dose. The need to investigate the feasibility of a White Irradiation Test setup at Elettra (WhITE), the Italian Synchrotron Radiation Facility, has been suggested by several reasons: the evaluation of vacuum performance of new materials to be used at Elettra, such as the Non Evaporable Getter coatings; the preconditioning of new vacuum components before their final installation; the evaluation of the efficiency of different cleaning pretreatments on vacuum components; the assessment of any interaction between the photon flux and the vacuum instrumentation. The use of an already installed "standard" Bending Magnet Front-End (BMFE) has been verified. It involves a remarkable saving in time and money and the BMFE can be easily recovered to standard operations (hosting a regular beamline), by just removing the irradiation arrangement. The installation of WhITE on a currently unused BMFE Left Branch Light Port has been considered. Only a minor modification on the Front-End itself is required: the insertion of a collimator in order to avoid low energy photons striking the conductance aperture. It can also be used to reduce the divergence of the photon beam hitting the sample. In this article we present the layout, current status and first results of WhITE.

VST2-ThP9 Measurements of Photon Stimulated Desorption from a Copper Beam Chamber after Complete Removal of Surface Oxide@footnote 1@*, C.L. Foerster,*** *C. Lanni,* Brookhaven National Laboratory

Photon Stimulated Desorption(PSD) was measured from a copper beam chamber after completely removing the vacuum surface oxide in order to reduce the PSD. Measurements of PSD and reflected specular photons were performed on NSLS beamline U9a at Brookhaven National Laboratory. PSD causes a pressure rise in accelerator and storage ring vacuum which limits their performance. For this experiment, a KEKB factory beam chamber from a previous experiment was chemically etched and chemically cleaned prior to installation on beamline U9a. Previous PSD measurements have shown that this chemical treatment removes any memory of prior exposure or conditioning. After installation, the copper chamber and end stop were vacuum baked to 250 °C for more than a week to completely remove vacuum surface oxides. The chamber was exposed to more than 1x10@super 23@ photons direct from the source having a critical energy of 595 eV and striking at an incident angle of 100 mrad. The major PSD yields for hydrogen, carbon monoxide, carbon dioxide, methane, and water are reported as a function of accumulated photon flux and preparation. The PSD yields for the copper chamber, after oxide removal, were found to be greatly reduced when compared to previous measurments at this laboratory and by those reported from other laboratories. @FootnoteText@ @footnote 1@Work performed under the auspices of the U.S. Department of Energy, under contract DE-AC02-98CH10886.

VST2-ThP10 Photon Stimulated Desorption from the Aluminum Surface with Water Vapor Exposure*, J.-R. Chen,*** Synchrotron Radiation Research Center and National Tsing-Hua University, Taiwan*; K.Y. Yang, J.Y. Yang,* National Tsing-Hua University, Taiwan*; G.-Y. Hsiung,* Sychrotron Radiation Research Center, Taiwan

The photon stimulated desorptions (PSD) from aluminum surfaces were studied. The aluminum samples, after the treatment of water vapor exposure, were irradiated by the synchrotron light with a critical photon energy of 2 keV. It was observed that the signal of H@sub 2@O gas was exponentially reduced during the synchrotron light irradiation. As the surface getting "dry", the phenomenon changed. In order to study the H@sub 2@O-PSD behavior, experiments were carried out with different conditions, such as different target bias, sample temperature, photon flux and photon dose. The experimental system, results and discussions are described in this paper.

VST2-ThP11 Study of Outgassing and Photon Stimulated Ion Desorption of Copper with Synchrotron Radiation*, Y.J. Hsu*, *C.-C. Lee, S.-H. Chang, G.-Y. Hsiung, J.-R. Chen,* Synchrotron Radiation Research Center, Taiwan

The surface characterizations of oxygen free copper by utilizing photoemission spectra (PES), thermal desorption spectra (TDS), photon stimulated ion desorption (PSID), and target current measurement with various surface treatments have been studied. In contrast to aluminum alloy, the XPS data showed the adsorbates on copper surface were apparently reduced after the surface annealing. In the PSID, copper showed the similar main ion desorption species as that of aluminum alloy while surface irradiated with synchrotron white light. However, the desorption yield of copper was much smaller than that of aluminum alloy. The desorptiom yield as a function of photon energy from 10 ~200 eV indicated ion desorption of copper were mainly excited by the generation of photoelectrons.

VST2-ThP12 Study the Photoelectron Yield for Al and Cu Materials*, G.-Y. Hsiung*, Synchrotron Radiation Research Center, Taiwan*; C.Y. Yang,* National Tsing-Hua University, Taiwan*; C.-C. Lee, Y.J. Hsu, J.-R. Chen,* Synchrotron Radiation Research Center, Taiwan

The photoelectron yield (PEY) from the Al and Cu materials is measured at the 19B beam line in SRRC. The surface of the test samples is treated by different methods, including the chemical cleaning, glow discharge cleaning, exposing water vapors, etc., prior to the photon irradiation. The alternate surface analysis by XPS, SIMS, TDS, etc. is applied to the samples for comparison of the various surface conditions relating to the PEY. The PEY for the unbaked samples is also compared. The results will be discussed.

Vacuum Science & Technology
Room 134/135 - Session VST3-ThP
Vacuum System Modeling Poster Session

VST3-ThP1 Pressure Distribution Modeling for Cyclotron's Vacuum Chambers and Ion Beam Guidelines*, A.V. Tikhomirov*, Joint Institute for Nuclear Research, Russia*; M.N. El-Shazly, G.G. Gulbekian,* JINR, FLNR, Russia

The simulation method for determination of the pressure distribution inside the vacuum chamber of any geometrical configuration for a cyclotron's vacuum system is described. The results of the simulation program codes tested on the base of the data obtained at the FLNR heavy ion cyclotrons are presented. The developed simulation method practically allows optimizing any configuration of the vacuum system from the point of view of the pumping speed and pump's location. In conjunction with another program code, developed by the authors for an evaluation of the ion charge changing cross section, this simulation method allows to forecast the ion beam loss due to the charge exchange with the residual gas molecules.

VST3-ThP2 Pressure Field in a Tube with General and Arbitrary Time- and Position-Dependent Degassing*, F.T. Degasperi*, Faculdade de Tecnologia de São Paulo FATEC-SP, Brazil*; S.L.L. Verardi,* Universidade de São Paulo, Brazil*; J. Takahashi, M.N. Martins,* Instituto de Fisica da USP, São Paulo, Brazil

We present in this paper analytical and numerical results for the pressure profile in a tube with general and arbitrary time- and position-dependent degassing. The time evolution of the pressure profile is discussed. We also study the time evolution of the pressure along the tube in situations commonly found in vacuum technology, like particle accelerators, colliders, storage rings, and synchroton light sources.

VST3-ThP4 Mathematic Simulation of Processes in Flow Parts of Hybrid Turbomolecular Vacuum Pumps*, M.G. Sapeshinsky*, Bauman Moscow State Technical University, Russia

Results on 3-dimensional mathematic simulation of processes in flow parts of hybrid turbomolecular pumps (TMP) are presented. Description of algorithms and of a calculation programs complex for characteristics of hybrid turbomolecular pumps with molecular and drum forcing channels is given. The influence of geometric parameters of a flow part on an operation rate and a maximal compression degree of pump channels is investigated. The concept of optimisation of hybrid pumps under restrictions of controlled parameters is developed.The optimal variants of a flow part are given. Rated and experimental data are compared. There is developed an algorithm of optimization of a TMP flow part with axial and axial-radial gas flow under functional restrictions on controlled parameters, ensuring the desired TMP operation rate at fixed suction pressure for a chosen gas, and also the desired operation rate for several gases using the algorithm of slipping access and the absolute penalty functions metod. It is found out, that within the investigated operation rate's range an axial-radial scheme has better mass-size characteristics compared to that of an axial scheme. Decrease in volume of a flow part with optimal geometric parameters makes from 36 % (S=0.5 m@super3@/sec) to 53 % (S=20 m@super3@/sec) due to decreasing the axial rotors number. Here the external diameter of axial rotors increased from 35 % (S=0.5m@super3@/sec) to 5 % (S=20m@super3@/sec). More preferable is the axial-radial scheme with periphery-center flow direction. It is found out, that if ensuring the desired raised evacuation characteristic for light gases, the flow part volume of all the three schemes increases due to increase in axial rotors number and smoother changing of geometric parameters over rotors, and mass-size charactericties of axial-radial schemes come worse. Decrease in the flow part volume comparing to that of an axial scheme makes for the scheme with periphery-center flow 24 % (S=20m@super3@/sec, P=10@super-5@ Pa, S=15 m@super3@/sec and P=10@super-3@ Pa). The volume of an axial scheme raised on 93 %, of axial-radial schemes - on 163 % and 150 % compared to the computation results when ensuring the desired operation rate only for nitrogen.

VST3-ThP5 Developing of Calculation Methods of Diffusion Vacuum Pumps' Characteristics*, M.G. Sapeshinsky,* Bauman Moscow State Technical University, Russia***; B.N. Kemenov,*** Npk Intelvac, Russia

Results on 3-dimensional mathematic simulations of processes in an inlet chamber of diffusion vacuum pumps, of interaction between pumped out gas and steam molecules are presented. Description of algorithmus and of a calculation programs complex for characteristics of diffusion vacuum pumps is given. Using the developed calculation programs the influence of parameters and form of a steam flow, geometry of a body, as well as of an oil reflector and protecting screens, on operation rate and on reverse oil flow of diffusion pumps is investigated. Rated and experimental data are compared. The concept of optimisation of an inlet chamber of diffusion pumps is developed

VST3-ThP6 Pressure Field Calculations in Vacuum Systems*, F.T. Degasperi,* Faculdade de Tecnologia de São Paulo FATEC-SP, Brazil*; S.L.L. Verardi,* IBILCE, UNESP, São José do Rio Preto., Brazil***; V. Baranauskas,*** UNICAMP, Brazil

The traditional and usual vacuum technology approach to the description of vacuum systems considers them made up of discrete elements. This approach is very useful, but it delivers only the average pressure, not allowing the evaluation of the pressure at each point of the vacuum system. In other words, the detailed pressure distribuition is not determined. In this article we study and describe a powerful method to deal with vacuum problems in the pressure field framework. It uses anlytical and computational tools based on the Finite Elements Method. Details of the mathematical formulation and modeling are given. In special, a detailed discussion about the boundary conditions is also presented. In this article we also calculate and show the pressure distribuition of complex geometries, considering degassing effects from the surfaces.

VST3-ThP7 Computer Applications in Vacuum Measurement*, D. Tian,* Lanzhou Institute of Physics, P.R.China

Study of vacuum measurement has been developed in our laboratory for over thirty years. Measurement standard apparatus of total pressure, partial pressure and flow (leak rate) were constructed successively. They are used to calibrate the vacuum gage, mass spectrometer, leak and flowmeter. Computer technology is used widely in these fields. With the aid of computer, these projects can proceed successfully and efficiently. Some application examples are introduced in this article. Computer simulation was used to solve some theoretical problems in vacuum measurement. By means of Monte-Carlo method and view-factor method the computer simulations were accomplished in nonuniform molecular flow field of dynamic flow method calibration system and relative calibration system. Computer can complete complicate scientific calculation easily. Static expansion apparatus is an absolute vacuum standard and needs a great deal of formula calculations for the correction of pressure, volume, and temperature. Computer can provide a real-time value of actual pressure so as to find measurement problems in time. In order to improve control accuracy, manual operation has been replaced by computer automatic control gradually. According to the principle of negative feedback and algorithm of proportional integral differential (PID) control, the fluctuation of pressure in variable chamber was controlled within ±0.01% by a computer adjusting the piston displacement. This technology enabled us to manufacture a high precise constant pressure flowmeter. Computer can not only control and safeguard vacuum pumps, valves and gauges, but also acquire and manage measurement data. Comparison method apparatus calibrates vacuum gages automatically with high efficiency by using interface communication and logical control. With further application of computer technology, vacuum measurement technology will progress rapidly in the future.

Applied Surface Analysis
Room 134 - Session AS-FrM

Catalysis and Surface Reactivity

Moderators: P.M.A. Sherwood, Kansas State University, K. Wandelt, Universitat Bonn, Germany

8:20am **AS-FrM1 Molecular Description of Surfaces of Transition Metal Oxide Catalysts**, ***J. Haber***, Polish Academy of Sciences, Poland **INVITED**

One of the fundamental fields of research is oxidation catalysis by transition metal atoms and ions (TMA, TMI), located at gas/solid oxide or liquid/solid oxide interfaces, because of its importance in chemistry, biochemistry and modern technology. When TM oxide is dispersed on a second oxide phase playing the role of a support, a number of phenomena may take place, as revealed by UPS, XPS, AES, STM, IR and Raman spectroscopies. The TM oxide may be dispersed on the surface in form of isolated TM-oxygen polyhedra, their clusters, a monolayer or small crystallites, the TMI may diffuse into subsurface layer to form solid solution, or may form surface bidimensional compounds. The type of the process will depend on chemical properties of both oxides, their surface free energies, type and structure of the support, method and temperature of preparation. The resulting surface electronic structure determines the conditions of the exchange of electrons between the reacting molecules of the catalytic reaction and the catalyst and hence the catalytic activity. The surface of a catalyst for selective oxidation must be tailored to perform complex multistep operations on reacting molecules, hindering interactions leading to unwanted byproducts. Active sites must be generated which could accelerate following elementary steps: - activate the hydrocarbon molecule, which should be adsorbed in a proper way, by abstraction of hydrogen from the selected site of the molecule; - inject or remove electrons from the surface intermediates by providing high density of states at the energy level corresponding to the C-H redox potential; - perform nucleophilic addition of a surface oxide ion of high enough basicity, which could be easily extracted from the surface in the desorption step of the oxygenated intermediate, e.g. by crystallographic shear mechanism; - enable rapid diffusion of hydrogen and its desorption as water; - easily reoxidize by interaction with gas phase oxygen.

9:00am **AS-FrM3 High-pressure XPS: A New Tool for the In-situ Investigation of Catalysts**, ***H. Bluhm***, *M. Haevecker, A. Knop-Gericke,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany*; F. Requejo, D.F. Ogletree, C.S. Fadley, Z. Hussain, M. Salmeron,* Lawrence Berkeley National Laboratory*; R. Schloegl,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

Photoelectron spectroscopy has been an extremely powerful tool in surface science for decades. It has been extensively used for the ex-situ characterization of catalysts' surfaces. Due to the short mean free path of electrons in a gas phase electron spectroscopies generally must operate in high vacuum. Traditional electron spectrometers are therefore not suited for the much needed characterization of catalytic surfaces under reaction conditions. To overcome these limitations, we have developed a new high-pressure electron spectrometer. Our setup utilizes a differentially pumped electrostatic lens system that refocuses the photoelectrons that are emitted from the sample (which is in a gaseous atmosphere of up to several torr) into the focal plane of a standard electron energy analyzer situated downstream, in the high vacuum region. Using this instrument we have investigated the methanol oxidation over a copper catalyst. The correlation of in-situ XPS spectra of the copper surface and the simultaneously obtained mass spectrometer data (that show the efficiency of the catalytic reaction, i.e. the turnover of the gas phase) allow us to draw conclusions about the electronic state of the catalyst under reaction conditions for the first time.

9:20am **AS-FrM4 XPS Analysis of Silica Supported Copper Catalysts for Fine Chemicals Synthesis**, *K. Wilson, A. Stewie,* University of York, UK*;* ***S.J. Hutton***, *A.J. Roberts,* Kratos Analytical, UK

Tightening legislation has led to a drive to develop new cleaner heterogeneously catalysed processes for the speciality chemicals industries.@footnote 1,2,3@ One major area of concern is the wide range of organic synthetic routes that currently rely on the use of inorganic or mineral acids. In recent years, metal trifluoromethanesulfonates or triflates have been reported as a new and interesting type of Lewis acid.@footnote 4@ These possess stronger Lewis acidity and higher water tolerances than their halide counterparts, which readily form the hydroxide or oxide.@footnote 5,6@ Recently we have discovered that silica supported Cu(SO@sub 2@CF@sub 3@)@sub n@ is an effective heterogeneous catalyst for the use in organic synthesis. We find that while silica supported catalysts exhibit high activity in phenol alkylation, versions supported on alumina or amine functionalised silica are relatively inactive. The origin of the high activity of Cu(SO@sub 2@CF@sub 3@)@sub 2@/SiO@sub 2@ has been investigated by high resolution XPS analysis of a range of supported and unsupported Cu(II) and Cu(I) salts to determine the oxidation state of the active Cu species. The copper 2p spectrum of free Cu(SO@sub 2@CF@sub 3@)@sub 2@ exhibits a main peak at 936.6 eV which has associated strong satellite transitions. In contrast, silica supported Cu(SO@sub 2@CF@sub 3@)@sub 2@ exhibits a single transition at 933.8 eV without the presence of intense satellite structures. This suggests that electron transfer from SiO@sub 2@ could be important in determining catalytic activity. @FootnoteText@ @footnote 1@ J.H. Clark, D.J. Macquarrie, Chem. Comm., 1998, 853. @footnote 2@ R. Sheldon, Chem. Ind., 1, 1997, 12. @footnote 3@ W.F. Hölderich, Stud. Surf. Sci. & Catal. 1993, 75, 127. @footnote 4@ S. Kobayashi, Chem. Lett., 1991, 2187. @footnote 5@ S. Kobayashi, Synlett, 1994, 689. @footnote 6@ K. Wilson, A. Renson, J.H. Clark, Cat. Lett., 1999, 61, 51.

9:40am **AS-FrM5 Effect of Surface Reduction on Decomposition of Dimethyl Methylphosphonate on Tungsten Trioxide Surfaces**, ***S. Ma***, *R.H. Jackson, B.G. Frederick,* University of Maine

The adsorption and decomposition of Dimethyl methylphosphonate (DMMP) on oxidized and reduced WO@sub 3@ surfaces have been studied with Calibrated Thermal Desorption Spectroscopy (CTDS) and X-ray Photoelectron Spectroscopy (XPS). XPS was used to characterize the surface by monitoring the valence band and W4f regions. The reduced surface, produced by Ar+ sputtering, contained a mixture of W@super 6+@ and W@super 5+@. Treatment of the surface in O2 at high temperature resulted in an oxidized surface. On the oxidized surface, desorption of methanol and dimethylether was detected, but only dimethylether was observed on the reduced surface. These products imply that the P-OCH@sub 3@ bond is broken to produce the methoxy intermediate during decomposition of DMMP on reduced and oxidized WO@sub 3@ surfaces. This mechanism is similar to the decomposition of DMMP on MgO and Al@sub 2@O@sub 3@ oxide surfaces.@footnote 1,2@ No phosphorus-containing compound was observed in CTDS. After CTDS experiments, XPS shows that phosphorus was left on the surface. The adsorption and desorption of methanol and dimethylether on the reduced and oxidized surfaces were compared with the production of these species from the DMMP decomposition. @FootnoteText@ @footnote 1@ M.K.Templeton and W.H.Weinberg, J. Am. Chem. Soc., 107 (1985) 97. @footnote 2@ Mark B.Mitchell, V.N.Sheinker and Eric A.Mintz, J. Phys. Chem. B, 101 (1997) 11192 .

10:20am **AS-FrM7 Auger Parameter Studies in Alloys of Transition Metals with Al or Mg**, ***M.-L. Abel***, *P. Tsakiropoulos, J.F. Watts,* University of Surrey, UK*; J.A.D. Matthew,* University of York, UK

Currently, alloys are designed either empirically or in a systematic and cost-effective way, which makes use of experimental and calculated phase equilibria (CALPHAD) data to select alloy composition with the desirable microstructures. The data obtained from this type of calculation are based on first principle calculations (FPC), but although phase diagrams predicted by FPC are topographically correct, they lack sufficient accuracy for practical applications. It is, therefore highly desirable to develop an experimental approach to the study of alloying behaviour. To produce alloys, a metallurgist usually considers the importance of such factors as the electronegativity difference or the atomic size mismatch in controlling the stability of metallic phases. The nature of alloying behaviour can be studied experimentally using the transfer of charge upon alloying. Quantification of charge transfer can be achieved using the Auger parameter and its variation over a wide composition range. This provides means of testing some of the predictions of FPC. In this work, transition metals have been selected because they form the basis of the constitution of conventional and development alloys. The aim of this research is to study hybridisation phenomena and the charge transfer between solvent and solute atoms in alloys. Changes of the Auger parameter determined from X-ray photoelectron experiments, is used as a tool to probe the electronic changes that take place as a result of alloying. The detection of the relevant Auger entries and core level energies is performed using the ESCA 300 in Daresbury (UK) which is fitted with a CrKb source. Core levels such as Si1s or Ti1s are then accessible and allow calculation of the Auger parameter of choice.

10:40am **AS-FrM8 Experimental and Theoretical Study of the Chemical Effects in the Auger Spectra of Aluminium, Copper and Carbon Compounds***, B. Timmermans, N. Vaeck,* ***F. Reniers,*** Universite Libre de Bruxelles, Belgium

The bonding and electronic structure information of surface atoms is most often studied by XPS, where the energy shift of a photoelectron peak can be ascribed to a change in the chemical environment. Because three atomic levels are involved in the Auger emission process, the use of Auger spectroscopy to obtain this information from peaks positions and line shape is more difficult. However, new progresses in signal analysis techniques make the extraction of most chemical information intrinsically present in the Auger spectra possible. The advantage of AES over XPS is its higher lateral resolution allowing the study of the surface distribution of the elements (Auger mapping), which, combined with modern computational methods, opens new opportunities in surface analysis. In order to try to correlate the changes in the Auger peaks with the changes in the chemical environment, we performed a full experimental and theoretical study of the Auger lines of aluminium, carbon and copper in several compounds. The changes in the peak energies and shapes were recorded in model spectra. Deconvolution of the peaks was achieved by factor analysis. The experimental results are compared to ab initio calculations based on a new cluster model including chemical, structural and relaxation effects. Al and C compounds, specifically, present important line shape modifications of valence Auger peaks that can be compared with calculations based on the knowledge of valence densities of states. These were obtained experimentally from XPS and theoretically from a full potential linearized augmented plane wave method within DFT. Further improvements came from accounting the final state hole-hole interaction by the well-known Cini-Sawatzky model.

11:00am **AS-FrM9 Investigation of Surface Oxides on Aluminum Alloys by Valence Band Photoemission***,* ***G. Claycomb****, P.M.A. Sherwood,* Kansas State University

This paper will address how core level and valence band X-ray photoelectron spectroscopy can be used to study the chemical composition of the surface films on aluminum alloys. Certain alloying elements may preferentially migrate to the surface, thereby altering the composition and consequently the chemistry of the surface. Magnesium and silicon are known to preferentially migrate to the surface of the 6061 aluminum alloy but the chemical nature of the films formed on the surface is not well understood. The surface films can be identified by core level and valence band X-ray photoelectron spectroscopy. It will be shown that the type of magnesium film formed at the surface can be determined by comparing the valence band spectra of the aluminum alloy surface with that of the model compounds, magnesium oxide, magnesium hydroxide and the magnesium aluminum oxide. The effect of boiling water on the surface film will be discussed. It will also be seen that valence band photoemisson spectra, interpreted by band structure calculations, is a very effective tool for the conclusive identification of the surface species present. This material is based upon work supported by Luxfer Gas Cylinder.

11:20am **AS-FrM10 Use of Core- and Valence-Band XPS to Measure the Differences Among Similar Oxide and Mineral Phases***,* ***F.S. Ohuchi****, G. Ghose,* University of Washington*; M.H. Engelhard, D.R. Baer,* Pacific Northwest National Laboratory

The three polymorphs of Al@sub 2@SiO@sub 5@, sillimanite, andalusite, and kyanite, are geologically important minerals. The differences in their stability relations depend critically on the differences in the chemical bonding of each polymorph of Al@sub 2@SiO@sub 5@, in which half of the Al-coordinations are 4-fold (tetrahedral) in sillimanite (stable at low P and high T), 5-fold (trigonal bipyramidal) in andalusite (stable at low P and high T), and 6-fold (octahedral) in kyanite (stable at low P and high T), whereas the other half of the Al atoms are in 6-fold (octahedral) and Si in 4-fold (tetrahedral) coordination in all three polymorphs. A challenge is whether we are able to measure such small differences using XPS technique, since bonding differences and electronic structures are fundamental to our understanding of their thermodynamical properties and stability relations. We have therefore undertaken an investigation using a state-of-the-art XPS system by measuring Al(2p), Si(2p), O(1s) core level spectra as well as valence band spectra. Introducing a novel charge neutralization technique, clear differences in each spectrum from three different polymorphs were identified, and the change in the valence band spectra were compared with ab-initio density of state calculations. This technique was further applied to other minerals, such as magnesium-silicates.

Biomaterials
Room 102 - Session BI-FrM
Biosensors

Moderator: A.T.A. Jenkins, University of Bath, U.K.

8:20am **BI-FrM1 Planar Membrane Assemblies and Waveguide Optics for Biomolecular Device Applications***,* ***S. Saavedra,*** University of Arizona **INVITED**

This talk will focus on creation and characterization of supramolecular architectures, composed of polymerized lipid bilayer membranes functionalized with proteins, for use in sensor transduction. Novel optical transduction techniques based on planar waveguide optics will also be discussed.

9:00am **BI-FrM3 TOF-SIMS Analysis of Nucleic Acid Biosensor Chips***,* ***H.F. Arlinghaus****, M. Ostrop, O. Friedrichs, J.C. Feldner,* Universität Münster, Germany

In recent years DNA-chip-technology has been a subject of growing interest for clinical diagnostics as well as for DNA sequencing and forensic. DNA-chips are based on the method of sequencing by hybridization (SBH), where unknown DNA fragments are hybridized to complementary oligodeoxynucleotides (ODN) which are immobilized on a solid surface in an array format. The main variables in SBH are the attachment of the nucleic acid sequences to a solid surface, the conditions for hybridization, and the detection of the hybridized DNA sequences. We have used TOF-SIMS to examine in detail the immobilization process of PNA/ODN and to investigate its ability to detect DNA-fragments hybridized to complementary PNAs. For this purpose we immobilized either silane SA-layers on silicon wafers or DTSP SA-layer on Ag or Au surfaces. PNA and DNA of different concentrations were then bound to these layers. Deprotenated (M-H)@super -@ signal of the different ODN and PNA bases as well as phosphate ions were used to monitor the ODN/PNA concentration. It was found that the immobilization process is strongly dependent on concentration and immobilization time. Under optimized conditions, PNA can be covalently bound to these surfaces. The homogeneity of the immobilized PNA depends on the evaporation time of the PNA solution. After optimizing the immobilization process, complementary and non-complementary DNAs were hybridized to the PNA biosensor chip. Hybridized DNA could be readily identified by detecting the PO@sub 2@@super -@ and PO@sub 3@@super -@ masses. A good discrimination between complementary and non-complementary sequences could be achieved. It can be concluded that TOF-SIMS is a very useful techniques for investigating the complexity of the immobilization and hybridization processes and that SIMS has the potential for providing a rapid method for DNA/RNA sequencing and diagnostics. .

9:20am **BI-FrM4 A "Label-Free" Microchip Array Based Protein-Binding Assay using Surface Plasmon Resonance Imaging***,* ***C.E.J. Dentinger****, D. Martin, P. Wagner,* Zyomyx, Inc.

We demonstrate a microchip array based antibody binding assay that relies on imaging surface plasmon resonance (SPR) for detection of protein binding. Since SPR is sensitive to the index of refraction near a gold surface this assay does not require the binding proteins to be labeled (e.g. fluorescently or with a radio label), making it a "label free" detection technique. For our imaging SPR assay we have developed a method of specifically immobilizing proteins on surfaces that resist non-specific protein adsorption. These surfaces consist of a gold substrate coated with an omega functionalized alkanethiol self-assembled monolayer (asymNHS). The succinimidic ester head group of this monolayer is then reacted with biotin-LC-PEO-amine to make a biotin-coated surface. This surface will bind streptavidin in a manner that leaves some of streptavidin's binding pockets open to immobilize a wide variety of biotinylated proteins. The asymNHS, biotin-LC-PEO-amine, and streptavidin layers are characterized with ellipsometry, and Fourier transform infrared reflection adsorption spectroscopy (FTIRRAS). The "label-free" assay is then performed by immobilizing biotinylated proteins in an array format and monitoring the different antibody-antigen interactions on this array by imaging SPR. We have shown that this surface will bind a second protein only to the areas where the biotinylated proteins are immobilized. We have also demonstrated that with our imaging SPR we have the ability to watch the binding assays in real time.

9:40am **BI-FrM5 Comparative Analysis of Immobilization Strategies for Antibodies and Their Fragments on Biosensor Surfaces***, **P. Peluso,** D. Wilson, D. Do, M. Venkatasubbaiah, H. Tran, P. Kernen, K. Witte, B. Heidecker, P. Wagner, S. Nock,* Zyomyx, Inc.

Advancement in the study of proteomics requires the development of microarray biosensors which possess a high degree of sensitivity. Towards this goal, strategies must be optimized to couple biomolecular capture agents to matrices at sufficient densities without compromising their binding properties. Using SPR and radioimmunoassay methods, we have examined the effect of different coupling chemistries on the binding activities of various antibodies and their corresponding Fab forms. Novel methods for attaching antibodies and Fab fragments to surfaces were employed and compared with random coupling procedures. In general, we found oriented attachment to better maintain the binding activity of these molecules. Moreover, oriented-Fab surfaces appear to exhibit the highest molecular density and binding activity. We further extrapolated these findings to performance within a microarray format utilizing a fluorescence-based sandwich assay.

10:00am **BI-FrM6 Electrostatically Assisted SPR: A New Method for DNA Mutation Detection***, **L.K. Wolf,** R.J. Heaton, A.W. Peterson,* Boston University*; R.M. Georgiadis,* Boston University, usa

Detection of DNA base-pair mutations is essential for the study and treatment of genetic disorders and disease. Present-day studies use DNA microarrays and fluorescently labeled probes for high-throughput mutation analysis. Recently, we have discriminated between matched and mismatched surface immobilized duplexes by evaluating surface coverage and hybridization kinetics with electrostatically assisted surface plasmon resonance (SPR).@footnote 1@ Here, we show that this method allows label-free in-situ detection of a single A-C base-pair mismatch in a 25-mer oligonucleotide duplex. We also apply electrostatically assisted SPR to other types of mismatches, demonstrating the generality and usefulness of this method to mutation detection. The effects of ionic strength on mismatch discrimination are also investigated. @FootnoteText@ @footnote 1@ R. J. Heaton, A. W. Peterson, and R. M. Georgiadis, Proc. Nat. Acad. Sci. 98, 3701 (2001).

10:20am **BI-FrM7 DNA Assay Sensitivity in the BARC Magnetoresistive Biosensor***, **M.A. Piani,*** NOVA Research, Inc.*; R.J. Colton, M. Miller, J.C. Rife, P.E. Sheehan,* Naval Research Laboratory*; C.R. Tamanaha,* Geo-Centers, Inc.*; L.J. Whitman,* Naval Research Laboratory

The Bead ARray Counter (BARC) biosensor uses DNA microarrays, magnetic microbeads, and giant magnetoresistive (GMR) magnetic field sensors to detect and identify biological molecules.@footnote 1@ The core of the sensor is a small, microfabricated chip containing an array of 64 GMR sensors. Distinct single stranded DNA capture probes are immobilized on each sensor. Complementary DNA in a sample is allowed to hybridize on the chip, and is then labeled with magnetic microbeads that are detected by the GMR sensors. The overall system sensitivity is a convolution of the chemical and GMR sensor sensitivities. The chemical sensitivity is determined by the effectiveness of the hybridization and labeling assay. Our current chemical sensitivity is 10 fM for a 60 minute hybridization of 30 bp oligonucleotides. Our efforts to improve this sensitivity involves two tracks. First, we are working with chemiluminescent assays in order to optimize the immobilization and hybridization steps. Second, we are experimenting with peptide nucleic acid (PNA) capture probes instead of DNA. PNA is a synthetic oligonucleotide analog with a neutral backbone that hybridizes with complementary DNA with a higher affinity then the DNA complement. Furthermore, PNA molecules are resistant to nucleases ("DNAses"), enabling the BARC chip to be reconstituted and reused following treatment with the enzyme. Our initial results with PNA indicate an increase in chemical sensitivity of one to two orders of magnitude. @FootnoteText@ @footnote 1@Edelstein et al., Biosensors & Bioelectronics 14, 805 (2000).

10:40am **BI-FrM8 Study of the Formation and Function of the Cell Membrane Hybrid Layers Containing G-Protein Coupled Receptors at SAM Surfaces***, **V. Silin,*** National Institute of Standards and Technology*; R. Madhusudhana,* Institute of Biochemical Research, India*; J.T. Woodward, K.D. Ridge, A. Plant,* National Institute of Standards and Technology

Cell membrane vesicles can reorganize at an alkanethiol/lipid mixed monolayers or alkanethiol monolayer-coated surface resulting in the formation of cell membrane hybrid (CMH) layers. The ability to form CMH layers at the surface from various cell types expressing G-protein coupled receptors offers a promising method for the rapid screening of potential membrane receptor ligands. In our work CMH layers were formed using membrane vesicles from monkey kidney COS-1 cells that had been transiently transfected with synthetic human CCR5 chemokine receptors. CMHs were formed on a thiahexa-(ethylene oxide)-octadecane (THEO-C18) thiol surface or on a mixed POPC/THEO-C18 surface. AFM and SPR technique showed that the membrane form continuous layers at the surfaces with a thickness around 4 to 5nm for different samples. CMH surfaces were tested using specific antibodies against CCR5 receptors to check the surface concentration of the receptors at the surfaces and their orientation. The specific binding of the chemokine ligand was detected at this surface over different concentration. The kinetics of the CMH formation, as well as antibody and ligand binding to the surfaces was measured using the SPR technique, which showed extremely good sensitivity for this application. A number of control experiments were carried out with nonspecific antibodies, ligands and membranes to support data for the specificity of the CCR5 receptor response.

11:00am **BI-FrM9 Surface Chemistry for a Membrane-based Biosensor@footnote 1@***, **C. Cole,*** Nova Research, Inc.*; M. Natesan,* Geo-Centers, Inc.*; M. Malito,* Nova Research, Inc.*; R.J. Colton, L.J. Whitman,* Naval Research Laboratory

A multianalyte biosensor has been developed that uses magnetic force to differentiate between specific and nonspecific ligand-receptor/ligand-surface interactions.@footnote 2@ The initial sensor was developed as a 36-well microtitre plate, using surface chemistries developed to modify polystyrene.@footnote 3@ In order to enhance sensitivity, reduce assay time, and increase portability, a second generation sensor is being developed that replaces the polystyrene with an alumina ultrafiltration membrane. Although the use of inorganic supports is not necessarily novel, the application of polymer coatings designed to reject protein adsorption to such a surface is. We have developed methods to introduce desired surface functionalities onto commercial membranes. At the same time, we have addressed the potentially more critical issue of ensuring that our coatings are highly reproducible, thus providing for a biosensor with consistent response. To supplement XPS, semi-quantitative methods have been developed to specifically determine the extent of poly(ethyleneimine) and poly(ethyleneglycol) coverage; resulting lots of derivatized surfaces have been found to be indistinguishable in assay use. The membrane-based biosensor has been used to detect proteins, bacteria, and viral particles in 25 minutes or less, with an enhancement in sensitivity of 2-3 orders of magnitude compared to the initial prototype (e.g., 10@super 3@ pfu/mL MS2 vs. 10@super 5@ pfu/mL on the plate-based sensor). Various arraying technologies are being evaluated, including photolithography with activated biotin, mechanical masking, and arraying through site-specific chemistry. Use of these technologies to produce an arrayed filter for multianalyte detection will be discussed. @FootnoteText@ @footnote 1@ Supported by the Joint Technical Panel for Chemical and Biological Defense @footnote 2@ Lee et al., Anal. Biochem. 287, 261 (2000) @footnote 3@ Metzger et al., J. Vac. Sci. Technol. A 17, 2623 (1999).

11:20am **BI-FrM10 An Electroactive Substrate for Direct Transduction of Biorecognition***, **J. Yan,** P. Hampton, G. López,* The University of New Mexico

Direct electrochemical transduction of biorecognition on well-defined and protein-resistant electrode surfaces has recently attracted enormous attention. Herein, we report the design and characterization of self-assembled monolayers (SAMs) presenting protein binding ligands, electroactive probe molecules and protein-resistant oligo(ethylene glycol) moieties that allow direct electrochemical transduction of biorecognition at modified electrodes. The electroactive compound, N-(11-mercaptoundecyl)-N'-carboxymethyl-4,4'-bipyridinium dibromide (1), was selected and synthesized because of the known environmental sensitivity and reversibility of the redox chemistry of the viologen groups (i.e., 4,4'-bipyridyl dications) and potential to derivatize the acid terminus with biological molecules. Mixed SAMs of compound 1 and (1-mercaptoundec-11-yl)tri(ethylene glycol) (2) on gold were prepared by coadsorption from a solution of 1 and 2 (@chi@@sub 2@ = 0.6). N-(5-aminopentyl)biotinamide was subsequently attached to the surface through amide bonds. Cyclic voltammetric, ellipsometric and X-ray photoelectron spectroscopic measurements confirmed the attachment of the biotin ligands and the efficiency of the SAM in preventing nonspecific protein binding. Incubation of the biotin-modified SAM in a phosphate buffered saline (PBS, pH 7.4) containing 30 µg/ml anti-biotin for 2 h resulted in a significant negative shift in the redox potential of viologen moieties and a decrease in the peak currents and the charging currents. Incubation of the biotin-modified SAM in PBS containing biotin-blocked anti-biotin for 2 h, however, showed no change in the redox potential, peak currents and charging currents, indicating that the adsorption was biospecific.

11:40am **BI-FrM11 Crystalline Bacterial S-Layer Proteins: A New Supporting Structure to Separate and Stabilize Lipid Membranes*, B. Schuster*,** *P.C. Gufler, D. Pum, U.B. Sleytr,* Universitaet fuer Bodenkultur Wien, Austria

A key component in the combination of membrane-associated molecular recognition mechanisms with inorganic surfaces is an ultrathin layer separating the lipid membrane and the solid surface. The demands on this layer are manifold as it should both, stabilize and maintain the fluidity and structural properties of the lipid membrane. This is an essential feature providing an environment for reconstitution and immobilization of membrane proteins under non-denaturing conditions. One promising strategy is the application of bacterial cell surface layers (S-layers) to support (bilayer) lipid membranes (BLMs). S-layer proteins are the simplest self-assembly systems that produce crystalline, nanometer-thick, isoporous lattices with well-defined topographical and physico-chemical properties. S-layer proteins have been recrystallized on solid supports like gold or silicon wafers, or deposited on porous polymer filters. Attached BLMs exhibit an increased fluidity compared to dextran- or silane-supported BLMs and the stability is significantly enhanced. By contrast with the less stable BLM on polymer filters, successful reconstitution of staphylococcal alpha-hemolysin was observed with BLMs separated by an S-layer from the porous support. The unitary conductance of a hemolysin pore was found to be similar reconstituted in S-layer supported BLMs on porous supports and in common folded BLMs. As an alternative to soft polymer cushions, to hybrid or tethered lipid membranes, S-layer supported lipid membranes provide a biomimetic, water-containing environment for transmembrane proteins. Furthermore, composite S-layer/lipid membranes in combination with new sensor technology might play an important role in the development of biosensors.

Electronics
Room 131 - Session EL+SE+TF-FrM
Laser Processing of Surfaces

8:20am **EL+SE+TF-FrM1 Laser Creation of 3D Micro- and Nano-objects: Processing, Properties and Applications*, M.J. Stuke*,** *M. Koch,* Max-Planck-Institut f. Biophys. Chemie, Germany*; A. Moore,* University of the Pacific*; K. Mueller,* Max-Planck-Institut f. Biophys. Chemie, Germany*; G. Padeletti,* CNR Monterotondo*; K. Williams,* Max-Planck-Institut f. Biophys. Chemie, Germany*; G. Fuhr,* Humboldt University, Germany **INVITED**

Recent results obtained by VUV laser ablation of organic fibers and by laser direct write of 3D microelectrode structures will be described with special emphasis on: (1) creation of a cage on a tip for touch-free trapping, handling and transfer of NEUTRAL objects in solution. Video sequences will give direct evidence for the new possibilities (2) ultraprecise machining of spider fibers, an ultrastrong material.

9:00am **EL+SE+TF-FrM3 Excimer Laser Surface Treatment for Aluminum Carbide Growth*, F. Fariaut,*** GREMI, France

The excimer laser process reported is developed to enhance the mechanical and chemical properties of aluminum alloys. It would be interesting to use aluminum alloys in the automotive industry widely because of their low density, corrosion resistance and good workability. The motor weight can be reduced by replacing usual materials such as iron-steel by light alloys treated to increase their wear resistance. Ceramic materials generally exhibit great strength, resistance to wear and oxidation. The use of laser beams allows surface treatment to be located at the parts strongly exposed to wear and friction. The surface undergoes a transformation leading to an increase in hardness without changing the dimensions of the piece, thus avoiding no remachining after treatment. The laser process is especially suitable for environment protection as there is no pollution by chemical solvent or emanation. An excimer laser beam is focused onto the alloy surface in a cell containing 1 bar propylene gas. A vapor plasma expands from the surface and shock wave dissociates and ionizes the ambient gas. It is assumed that carbon from plasma in contact with the surface penetrates in depth. Thus it is necessary to work with a sufficient laser fluence to create the plasma, but this fluence must be limited to prevent laser-induced surface roughness. The carbon concentration profiles are determined from RBS and SEM coupled to EDX analysis. Crystalline quality is evidenced by XRD technique. TEM gives the in-depth microstructure. Fretting coefficient measurements exhibit a lowering for some experimental conditions. The polycrystalline cemented layer obtained is several micrometers thick and composed of a pure composition (columnar microstructure) top layer (200-500nm thick) standing on a diffusion layer (grains). This layer allows a significant decrease in the fretting coefficient.

9:20am **EL+SE+TF-FrM4 Laser Surface Treatment for Corrosion Prevention*, C. Georges*,** *N. Semmar, C. Boulmer-Leborgne,* GREMI, France*; C. Perrin, D. Simon,* CERI, France

The materials used in electrical contact applications are constitued of a copper alloy (brass or bronze) covered with nickel coating (diffusion barrier) and with a gold coating. There are some porosities in the nickel and gold layers which induced corrosion of the underlying layers. To modify structure of gold coating, some laser surface treatments have been undertaken. An excimer laser is used as the photon absorption coefficient is larger in UV range and because the laser beam homogeneity is available for a surface treatment. The purpose of this surface treatment is to suppress the porosities of the gold layer which are responsible of the corrosion pits and to smooth the surface as the roughness bothers a correct electrical contact. The effects of the laser treatment are studied according to different surface parameters (roughness and composition of the substrate, thickness and composition of the gold coating). The laser beam parameter influence on surface melting is simulated by numerical code. Tests of corrosion are carried out in the humid synthetic air containing low contents of pollutants (NO2, SO2 and Cl2). The technique used to control these effects are : optical microscopy, SEM, grazing X-rays and ESCA. One dimension heat conduction is resolved to simulate the temperature time evolution and the melted depth as a function of the laser parameters (laser fluence, pulse time duration). This modelling helps to the understanding of mechanisms for laser interaction with the connector surface and will allows to determine the laser type to use for this appication.

9:40am **EL+SE+TF-FrM5 Laser Processing Opportunities with a High Average Power Free Electron Laser*, H.F. Dylla*,** *S.V. Benson, J. Boyce, G. Biallas, D. Douglas, G.R. Neil, R. Evans, A. Grippo, J. Guebeli, K. Jordan,* Jefferson Lab*; M.J. Kelley,* Jefferson Lab and College of William and Mary*; R. Li, L. Merminga, J. Preble, M. Shinn, T. Siggins, R.W. Walker, G.P. Williams, B. Yunn,* Jefferson Lab

A kilowatt class free electron laser has been operational at Jefferson Lab since 1999. The associated user facility laboratories are being used for laser-materials studies that take advantage of the FEL's high average power, broad tunability and sub-picosecond pulse structure. The presently operating FEL delivers kilowatt level powers over the mid-infrared (3-7 microns). Recently, the device has extended operation through the visible (at the 100 watt level) and the UV (at the 10 watt level) through harmonic generation. A major upgrade is currently under way that will increase the power level in the IR to 10 kW and extend kilowatt operation through 300 nm in the UV. FEL users involved in materials processing have demonstrated unique applications involving: pulsed laser deposition, laser nitriding, laser production of carbon nanotubes, laser ablation and laser micromachining.-This work supported by the Office of Naval Research, the Commonwealth of Virginia, DOE Contract DE-AC05-84ER40150, and the Laser Processing Consortium.

Electronics
Room 124 - Session EL-FrM
ULSI Metallization & Interconnects

Moderator: D. Temple, MCNC

8:20am **EL-FrM1 Copper Alloys for Interconnections in Microelectronics*, J.M.E. Harper*,** *C.K. Hu,* IBM T.J. Watson Research Center*; K. Barmak,* Carnegie Mellon University **INVITED**

We review the attributes of copper alloys which are suitable for consideration in silicon chip interconnections. Many properties of copper improve with the addition of alloying elements, including corrosion protection, electromigration resistance and mechanical stability. However, these gains must be balanced against the inevitable increase in resistivity caused by adding impurity atoms. Alloying elements will be classified into three types of immiscible systems, plus systems in which Cu compounds form. We focus on alloy systems in which the resistivity can be lowered to that of almost pure Cu within a maximum processing temperature of about 400 @supero@C. In addition, the constraints of sub-250 nm dimensions on alloy precipitation and microstructure evolution will be summarized. It will be shown that there are promising strategies for incorporating alloys into copper interconnections.

9:00am **EL-FrM3 Microstructure Evolution and Interfacial Reactions in Cu-Mg Alloy Films on SiO@sub 2@*, M.J. Frederick*,** *R. Goswami, G. Ramanath,* Rensselaer Polytechnic Institute

Copper is currently the preferred interconnect metal in microelectronic devices due to its high electrical conductivity and electromigration resistance. Alloying Cu with a few at.% Mg has been shown to inhibit Cu diffusion into SiO@sub 2@, promote adhesion to adjacent dielectric layers (presumably through interfacial phase formation), and increase electromigration resistance without significant decreases in conductivity. It has also been reported that Mg promotes a (002) preferred orientation. Here, we investigate mechanisms of microstructure evolution and interfacial reaction pathways in sputter-deposited Cu-Mg alloy films during annealing. We combine in situ resistivity measurements with ex-situ Rutherford backscattering spectroscopy (RBS), plan-view and cross-sectional transmission electron microscopy (TEM), and X-ray diffraction (XRD) to characterize grain size and orientation evolution, interfacial segregation and phase formation. The effects of Mg precipitation, interfacial segregation, and phase formation at the Cu/SiO@sub 2@ interface, and their influence on grain size and preferred orientation are revealed for nominal Mg supersaturations from 0 to 15 at.%. We also present preliminary results on Mg/SiO@sub 2@ structures to reveal interfacial phase formation, and epitaxial Cu-Mg(001) alloy films to the isolate effects of alloying on evolution of grain size and preferred orientation.

9:20am **EL-FrM4 An Investigation of Compound and Non-compound Forming Dilute Binary Cu-Alloy Thin Films*, A. Gungor*,** *K. Barmak,* Carnegie Mellon University*; C. Cabral, C. Lavoie, J.M.E. Harper,* IBM T.J. Watson Research Center

The control of microstructural features such as grain size and texture in very narrow copper interconnections is increasingly important as dimensions reach the 100 nm range. This is because the resistivity must be minimized, yet other properties including adhesion and resistance to void formation need continued improvement, which will require alloying additions to copper. We have undertaken a detailed investigation of dilute binary Cu alloy films, and in this paper we report on six systems, three of which, Cu-Al, -In, and -Ti, are compound forming and the other three of which, Cu-Ir, -Nb, and -W, are non-compound forming. We find that annealing results in the lowest resistivity and the strongest fiber texture in Cu(Ti), while the largest grain size is seen in Cu(In) films. In addition, in previous work@footnote 1@ we have shown that the dissociation mode of the non-compound forming alloys can be categorized using the Cu-rich end of the respective binary phase diagrams and the resistance-temperature behavior of the alloy films. Based on this classification scheme, we will show that Cu-W belongs to category III since its resistance-temperature plots show multiple drops as seen for other alloys in this category, while Cu-Ir belongs to category II. The classification of Cu(Ir) is based on its high temperature behavior, whereby the resistance increase is a result of solute re-dissolution and not a result of agglomeration. @FootnoteText@ @footnote 1@ K. Barmak, G. A. Lucadamo, C. Cabral, Jr., C. Lavoie, and J. M. E. Harper, J. Appl. Phys.87, 2204 (2000).

9:40am **EL-FrM5 Interfaces in Copper Nanoconnections***, P. Heino,* ***E. Ristolainen,*** Tampere University of Technology, Finland

Miniaturization of electronic devices leads to nanoscale structures in the near future. Mechanics of these nanostructures and their connections are not well understood, since the surfaces and interfaces play a major role at nanoscale. As the metallization and interconnect material copper seems to be the technological choice, mainly due to its low electrical resistance. In copper metallization, a barrier layer between copper and the rest of the system is needed to prevent diffusion and to have enough adhesion. In such disordered systems, the interfaces are often the weakest spots. To conclusion, the interfaces are the most important parts to study. Tantalum seems to be one of the most common barrier metals, and two different interfaces are formed in the Cu-Ta-Si system. We use molecular dynamics with embedded-atom or modified embedded-atom potentials as means. At the Cu-Ta interface, a strong positive correlation is found between energy and strength indicating those low-energy interfaces is weak. More details of the results from the Ta-Si system will be discussed at the conference.

10:00am **EL-FrM6 Cu Film Deposition under Low Energy Cu Ion Bombardment*, K. Miyake,*** Saitama University, Japan*; Y. Ishikawa, L. Won, M. Isshiki,* Tohoku University, Japan*; M. Yamashita,* Seinan Industries Co., Ltd., Japan

It is well known that low energy ion bombardment during film growth enhances surface atom migration and as a result film properties are much improved. We investigated Cu film deposition under low energy Cu ion bombardment using non-mass separated ion beam deposition system. To produce Cu ions we developed an RF excited Cu ion source, which is composed of Cu RF coil and high purity Cu rod target located in the center of the coil. An argon plasma was initially generated in the RF coil(pressure: 1 Pa, RF power: 200 W) and then, the Cu target was DC (1 kV) sputtered in the Ar plasma to generate sputtered Cu neutrals and Cu vapor. These Cu neutral particles were effectively Penning ionized in the Ar plasma and were converted to Cu ions. By applying negative bias voltage(-150 V) to a Si substrate, Cu films were deposited on the Si substrate at RT under 150 eV (or less due to collisions) Cu ion bombardment. Very fine grained Cu films were obtained by applying 150 eV bias voltage to the substrate. Film properties including microcrystalline structure, packing density, electrical resistivity, preferred orientation Cu(111), etc. were improved compared with the case of no substrate bias. The effect of low energy ion bombardment on these improvements will be discussed.

10:20am **EL-FrM7 Conductivity Issues with Cu at sub-100 nm Dimensions*, S.M. Rossnagel,*** IBM T.J. Watson Research Center*; C. Inoki, T.S. Kuan,* SUNY-Albany

At thicknesses or dimensions at or well below 100 nm, Cu resistivity increases significantly. The primary issues are the so-called size effect (scattering from surfaces), grain boundary scattering and orientation effects, surface roughness, and impurities. In addition, diffusion barriers will have a negative effect due to displacement of Cu layers. Measurements on polycrystalline and single crystal Cu films and some features down to 20 nm show resistivity increases as-high or higher than predicted, indicating diffuse electron scattering at surfaces. Varying the surfaces of the Cu, either the roughness or the composition of overlayers, shows some positive effects at limiting the large effect of the scattering. In addition, the size effects of other materials, such as Au and Al, indicate that at sub-40 nm dimensions, Cu may no longer be desireable.

10:40am **EL-FrM8 Cu ECD: Modeling the Effects of Additives*, S. Sen,*** Rensselaer Polytechnic Institute*; S. Soukane,* Applied Materials*; T.S. Cale,* Rensselaer Polytechnic Institute

Plating additives used in Cu ECD undergo complex reactions that are not well understood but are important to know for the optimization and control of these processes. Simulation results are presented on feature scale modeling of Cu ECD in the presence of additives, incorporating chemistry based models to describe the additive action. We consider an electrolyte bath with three species; cupric ions and two additives. One additive accelerates the copper deposition reaction and results in bump formation on the top and the second additive suppresses deposition at the feature mouth, resulting in more uniform deposition rates in the entire feature. The cupric ion reacts by a two-step charge transfer reaction described by Butler-Volmer kinetics. The accelerator kinetics is described following Moffat.@footnote 1@ The accelerator reacts catalytically with the cupric ions on the electrode enhancing the charge transfer reaction. Additionally the species coverage increases as the surface shrinks due to growth, increasing the deposition rate. The leveling agent adsorbs onto the electrode, occupying active sites and inhibiting copper deposition.@footnote 2@ It is used in the mass transfer limited regime, hence the inhibition is lower in the feature interior than at the top, resulting in more uniform deposition profiles. Feature scale simulations are done with the ECD module of EVOLVE,@footnote 3@ which has transient and steady state solvers for the governing diffusion-reaction equations, and allows inclusion of chemistry based models for the component reactions. @FootnoteText@ @footnte 1@T. P. Moffat, D. Wheeler, W. H. Huber and D. Josell, Electrochemical and Solid-State Letters, 4(4), pp. C26-C29, (2001). @footnote 2@S. Soukane and T. S. Cale, Proceedings of the Seventeenth International VLSI Multilevel Interconnections Conference (VMIC), Tom Wade, ed., IMIC, 2000, pp. 260-262. @footnote 3@EVOLVE is an extensible topography simulation framework. EVOLVE 5.0i was released in June 1999. Copyright 1990-2000, Timothy S. Cale.

11:00am **EL-FrM9 Comparison of TiN, TaN, and WN@sub x@ as Diffusion Barriers for Copper on Silicon Dioxide: Thermal Annealing and Bias Temperature Stress Tests***, H. Kizil,* ***C.O. Steinbrüchel,*** RPI

The stability of TiN, TaN, and WN@sub x@ as diffusion barriers for Cu on silicon dioxide has been investigated using capacitance-vs-voltage (C-V) and leakage current-vs-voltage (I-V) measurements as a function of thermal annealing and bias temperature stress (BTS) conditions. Samples consisted of MOS capacitors with a film stack of 300 nm Cu/barrier/25 nm thermal silicon dioxide on Si. The barrier thickness was 5, 10, or 20 nm. The WN@sub x@ was investigated at two different compositions. Compositional depth profiles were taken with XPS and SIMS. Samples were pre-annealed in Ar/3% hydrogen for 30 minutes at various temperatures. BTS tests were performed at 2 MV/cm and 150, 200, and 250 °C, for periods of up to one hour in flowing nitrogen. The main results can be summarized as follows: In order for BTS to yield negligible C-V flat-band voltage shifts, pre-annealing at 350 °C is necessary. This produces a substantial number of initial leakage current failures (i.e. before BTS) with TiN, but not with the other barrier materials. The leakage current in I-V tests is a much better test for barrier integrity than the flat-band voltage shift (or the absence thereof), in the sense that samples with minimal shifts in the C-V plots may still give unacceptably high leakage currents. TaN and WN@sub x@ consistently behave better than TiN under all stress conditions. The effect of oxygen in the barrier and at the Cu/barrier interface is also discussed.

11:20am **EL-FrM10 Low-Temperature CVD of ZrB2 and CrB2 Metallic Ceramic Thin Films***,* ***E.J. Klein****, D.-Y. Kim, G.K. Windler,* University of Illinois at Urbana-Champaign*; J.-H. Sung,* Novellus*; D.M. Goedde,* Intel*; G.S. Girolami, J.R. Abelson,* University of Illinois at Urbana-Champaign

Transition metal diborides are classified as "metallic ceramics" due to their high mechanical hardness, chemical stability, melting temperature and electrical conductivity. This combination of properties makes them attractive as diffusion barrier materials for the contact metallization in next-generation microelectronics or wide bandgap semiconductors. We report the low-temperature chemical vapor deposition of fully conformal ZrB2 and CrB2 thin films with essentially bulk properties. ZrB2 films are deposited at a substrate temperature of 300 C using the single-source precursor Zr(BH4)4 and a concurrent flux of atomic hydrogen produced by a remote hydrogen plasma source. The films have a B/Zr ratio of 2, electrical resistivity of 40 micro-ohm-cm, and appear amorphous in X-ray diffraction. By contrast, films grown without the use of atomic hydrogen are B-rich, oxidize rapidly in air, and have high resistivity; we will show using mass spectroscopy that the role of atomic hydrogen is to enhance the removal of excess boron from the growth surface as B2H6. A 20 nm thick stoichiometric ZrB2 film deposited onto doped c-Si(001) has a low contact resistivity and is an excellent diffusion barrier: a Cu film deposited by PVD onto the ZrB2 does not interdiffuse with Si after annealing for 30 minutes at 750 C. CrB2 is deposited by CVD at 300 C without atomic hydrogen using the new precursor Cr(B3H8)2, which we synthesized in our laboratories and report for the first time. We will report preliminary results on the composition, electrical, and diffusion barrier properties of CrB2 films.

Magnetic Interfaces and Nanostructures
Room 110 - Session MI+SS-FrM

Magnetic Thin Films and Surfaces II

8:20am **MI+SS-FrM1 Novel Spin Structures in Fe@sub 3@O@sub 4@/CoO and Fe@sub 3@O@sub 4@/NiO Superlattices***,* ***Y. Ijiri,*** Oberlin College*; J.A. Borchers, R.W. Erwin, S.H. Lee, K.V. O'Donovan,* National Institute of Standards and Technology*; P.J. van der Zaag, L.F. Feiner, R.M. Wolf,* Philips Research Laboratories*; D.M. Lind, P.G. Ivanov,* Florida State University **INVITED**

Using polarized neutron scattering methods, we have probed the magnetic ordering in MBE-grown Fe@sub 3@O@sub 4@/CoO and Fe@sub 3@O@sub 4@/NiO superlattices. Despite significant differences between the spinel ferrite and the rock salt monoxides, it is possible to grow high-quality epitaxial structures for these materials as a result of good oxygen sublattice matching. We have observed for these superlattices substantial changes in the spin structures for both the ferrimagnetic Fe@sub 3@O@sub 4@ and the antiferromagnetic monoxide (CoO or NiO). In particular, we have found new magnetic easy axes along with significant differences in the polarization characteristics for these thin films. The unusual structures are discussed in terms of the role of strain and exchange coupling between disparate magnetic materials.

9:00am **MI+SS-FrM3 Surface Structure and Phase/Orientation Control of Manganese Nitride Grown by Molecular Beam Epitaxy***,* ***H. Yang****, H.A.H. Al-Brithen, A.R. Smith,* Ohio University*; R.L. Cappelletti, J.A. Borchers, M.D. Vaudin,* National Institute of Standards and Technology

We have investigated the growth of manganese nitride on MgO(001) substrates using molecular beam epitaxy (MBE) and have studied the surfaces using scanning tunneling microscopy (STM). Manganese nitride has many bulk phases (labeled @theta@, @eta@, @zeta@, and @epsilon@). Using MBE, we can individually select these phases by controlling the growth parameters. For example, at low Mn flux, we obtain the N-rich @theta@ phase (MnN), which has fct structure;@footnote 1@ but at increased Mn flux, we obtain the less N-rich @eta@-phase (Mn3N2) which is also fct but includes ordered arrays of N vacancies, according to a model proposed by Kreiner and Jacobs.@footnote 2@ Neutron scattering confirms that the Mn moments are aligned in a layered antiferromagnetic arrangement. By adjusting the growth parameters, we are able to control not only the phase, but also the crystalline orientation. At low Mn flux, the @eta@-phase has its c-axis perpendicular to the growth surface (@eta@1). But at yet higher Mn flux, the c-axis is oriented parallel to the surface (@eta@2), a consequence being two equivalent domains, D1 and D2, at 90° to each other. These domains are evident during growth via RHEED, which shows two closely spaced 1st-order streaks due to the fct structure. Also, 1/3-order lines are observed due to the periodic vacancy planes which are normal to the surface. STM images following growth clearly reveal the two domains at the @eta@2 surface. Row structures corresponding to the vacancy planes are clearly observed. Atomic resolution images show enhancement for the Mn atoms at the intersections of the surface and vacancy planes. This is likely related to the fact that these Mn have fewer N neighbors compared to other surface Mn atoms. This work is supported by NSF. @FootnoteText@ @footnote 1@ Suzuki et al., J. Alloys and Compounds 306, 66 (2000), @footnote 2@ Kreiner and Jacobs, J. Alloys and Compounds 183, 345 (1992).

9:20am **MI+SS-FrM4 Mesoscopic Magnetic Structures Grown by Self-organization***,* ***J. Kirschner*****,** Max-Planck-Institut fuer Mikrostrukturphysik, Germany **INVITED**

Mesoscopic magnetic structures play an increasingly important role in magnetic storage technology, magnetic sensors, non-volatile random access memories, and "magneto-electronics" in general. Lithography-type processes for making such structures, though having been quite successful, will not be addressed in this talk. Rather, typical surface science approaches, involving adsorption, surface diffusion, epitaxial growth phenomena, and self-organisation will be exploited to produce and characterize mesoscopic magnetic structures. For example, magnetic wires may be made by step edge decoration on stepped single crystal surfaces by tuning surface diffusion. They form chains of long segments, connected by weak links. These structures resemble Ising chains, with magnetic properties determined by a gradual approach to thermodynamic equilibrium. Magnetic dots may be created by exploiting localized adsorption on reconstructed surfaces. It will be demonstrated, how magnetic pillars with a height-to-diameter ration of 2:1 can be grown on such a template and that such structures may perhaps overcome the "superparamagnetic barrier" in magnetic storage technology.

10:00am **MI+SS-FrM6 Direct Observation of Orbital Kondo Resonance on the Cr(001) Surface***, O.Yu. Kolesnychenko, R. de Kort, M.I. Katsnelson, A.I. Lichtenstein,* ***H. van Kempen,*** University of Nijmegen, The Netherlands

Scanning Tunneling Microscopy (STM) is an excellent tool to explore many-body phenomena, such as the formation of the Kondo resonance@footnote 1@. In addition to``classical'' Kondo effect, many-electron resonances have been theoretically predicted for scattering centers with non-spin degrees of freedom. Here, we will present the first direct evidences for the existence of orbital Kondo resonance on a transition metal surface. Low-Temperature STM and STS investigations were performed on the atomically clean Cr(001). The Cr(001) surface was produced by cleavage of a 99.99% Cr single crystal in situ at 4K. As we found out, the cleavage of Cr single crystals produce atomically flat and clean (001) surfaces. The STS investigations of the Cr(001) surfaces showed a very narrow resonance at 26 meV above the Fermi level. We found that at bias voltages corresponding to the resonance energy a cross-like depressions centered around impurities appears. This cross-like feature is a fingerprint of the orbital symmetry of the resonance analogous, for example, to the visualization of a superconducting gap near a zinc atom@footnote 2@. Although the resonance in the Cr(001) surface density of states has been observed previously at room temperature@footnote 3@ and was interpreted as a one-electron surface state, we are going to present additional experimental data which strongly indicate that the observed state on the Cr(001) surface is a many-electron orbital Kondo resonance which is formed by two degenerate spin-split d@sub xz@, d@sub yz@ surface states. We also carried out calculations for the periodic degenerated Anderson model which confirm the existence of the orbital Kondo resonance on the Cr(001) surface. @FootnoteText@ @footnote 1@ H.C. Madhaven, et.al., Nature 403, 512 (2000). @footnote 2@ S.H. Pan. et.al., Nature 403, 746 (2000). @footnote 3@ J.A. Stroscio, et.al., Phys. Rev. Lett. 75, 2960 (1996).

10:20am **MI+SS-FrM7 High Dipolar Magnetic Moment Observed on Ni/Cu(111) Nanostructures by Magnetic Circular X-ray Dichroism***, **C. Boeglin**, S. Stanescu, S. Cherifi,* IPCMS-CNRS, France*; A. Barbier,* CEA/DRFMC, France*; N.B. Brookes,* ESRF, France*; P. Ohresser,* LURE-CNRS, France*; J.P. Deville,* IPCMS-CNRS, France

The correlation between ultrathin film growth, structure and morphology and the induced magnetic properties is of fundamental interest in order to improve the theoretical understanding of magnetic properties in ultra-thin films. We report here growth and morphology studies at the first stages of growth of Ni on a Cu(111) single crystal substrate. This work has been performed by in-situ Auger, RHEED and STM at room temperature. The morphology shows in the early stages of the growth that nickel induces 10-30 nm large triangular islands monolayer in height. In addition stripes are formed at the step edges via a step flow growth mode. The particular shape of the oriented triangular islands has been examined by STM and segregation of Cu atoms could be evidenced on top of the Ni islands after 0.5 ML deposition. It is shown that the Ni morphology and the Cu diffusion both have a strong influence on the magnetic properties. Correlations have be evidenced by performing in-situ Magnetic Circular X-ray Dichroism studies on Ni/Cu(111) ultra-thin films. The evolution of the island size during the growth can be correlated with the evolution of the orbital magnetic moment whereas strong dipolar magnetic moments are related to the formation of a second Cu/Ni interface. Moreover, the in-plane orbital magnetic moment anisotropy has been measured and related to magnetocrystalline effects in the film.

10:40am **MI+SS-FrM8 Relating Magnetic and Structural Changes of Thin FeNi Alloy Films on Cu(100)***, **M. Hochstrasser**, J.G. Tobin,* Lawrence Livermore National Laboratory*; S.A. Morton, G.D. Waddill,* University of Missouri-Rolla*; F.O. Schumann,* Freie Universität Berlin, Germany*; N.A.R. Gilmann, R.F. Willis,* The Pennsylvania State University

At a concentration of around 65% Fe, bulk FeNi alloys exhibit the "Invar effect", a sudden arresting of the Wigner-Seitz cell volume and a zero expansion coefficient. Simultaneously, the crystal structure changes from face-centered cubic to body-centered cubic while the Curie temperature goes to zero. This structural transformation can be arrested in ultrathin alloys films grown epitaxially on a Cu(001) substrate. Theoretical work predicts that the fcc phase can exist in two possible states: a ferromagnetic high volume state or a antiferromagnetic low volume state (2@gamma@ state model) and a volume change between the paramagnetic and the high spin state of ~7%, and 1% change between a non-collinear equilibrium state and the high spin state. Experimental work shows a lattice expansion increasing linearly up to 3% at 65% Fe content followed by a sudden relaxation of 2% with increasing Fe content. The initial volume increase is associated with increasing magnetization/magnetic moment & spin alignment in the Ni-rich alloys. As the alloy is cooled below T@sub C@ (or a strong external magnetic field is applied), an increasing alignment of the magnetic moments causes the nearest-neighbor spins to push apart producing an internal pressure which expands the lattice. With increasing Fe content, this effect increases due to the increasing number of Fe nearest neighbors with the larger atomic magnetic moments. Eventually, a critical limit is reached (~65% Fe), when a magnetic/lattice volume instability develops. W ith x-ray magnetic dichroism the changes in the elemental magnetic moments were tracked. Spin polarized photoemission studies record a sudden decrease in the "mean-field" exchange splitting of the d-states with increasing Fe content through the critical "Invar transition". Angle-resolved photoemission imaging of states at the Fermi level reveal a much smaller splitting of the sp-states, which also tracks the changing magnetization with changing composition.

11:00am **MI+SS-FrM9 The Structure of Ferromagnetic Ultrathin Fe Films on Cu(100) is not fcc***, A. Biedermann, R. Tscheliessnig, M. Schmid, **P. Varga**,* TU Vienna, Austria

Ultrathin Fe films on Cu(100) are an ideal model system to study martensitic fcc-bcc phase transitions in Fe.@footnote 1@ Ultrathin Fe films on Cu are also distinguished by the appearance of a novel ferromagnetic phase which showed distinct fcc-like features in p revious electron diffraction experiments. By means of scanning tunneling microscopy we were able to reveal this phase as a novel "nanomartensitic" phase with the Fe atoms forming localy a bcc like structure @footnote 2@. This shows that the assumption of a ferromagnetic fcc phase is not necessary to explain the ferromagnetism observed in these films. @FootnoteText@ @footnote 1@ A. Biedermann, M. Schmid, and P. Varga, Phys. Rev. Lett. 86 (2001) 464-67 @footnote 2@ A. Biedermann, Rupert TschelieÃŸnig,M. Schmid, and P. Varga, Phys. Rev. Lett., submitted

11:20am **MI+SS-FrM10 Angle Resolved Auger Spectra of Ultrathin Fe on Gd (0001)***, **J.P. Nibarger**, D.P. Pappas,* National Institute of Standards and Technology

The in-plane to out-of-plane spin-reorientation phase transition of ultrathin Fe on Gd (0001) has been measured recently.@footnote 1@ Theoretical work has indicated the need for six-fold symmetry of the ultrathin Fe film in order to fit existing data on the spin-reorientation phase transition.@footnote 2@ Fe films consisting of 1.5 atomic layers on bulk Gd do no exhibit any long range ordering as determined by low energy electron diffraction. Angle resolved Auger electron spectroscopy (ARAES) will be used because it is sensitive to local order on the atomic scale and will determine the local symmetry of the Fe atoms. ARAES spectra will be shown that demonstrate the extent of six-fold symmetry in these films. @FootnoteText@ @footnote 1@ C.S. Arnold et al., Phys. Rev. Lett. 83, 3305 (1999). @footnote 2@ A.P. Popov, private communication.

11:40am **MI+SS-FrM11 Transverse Magneto-optical Kerr-effect in the Soft X-ray Regime at Iron and Cobalt Films on W(110)***, **J. Bansmann**, V. Senz, A. Kleibert,* University of Rostock, Germany

Tunable soft X-ray radiation opens the possibility for investigating element-specifically the magnetic properties of thin films, islands, and nanoparticles on surfaces. Well-known techniques are magnetic dichroism in photoemission (MDAD) and X-ray magnetic circular dichroism in photoabsorption (XMCD). However, magnetic phenomena can also be studied using the transverse Magneto-optical Kerr effect (T-MOKE) at the core levels of ferromagnetic materials using linearly polarized radiation. We will present new data using T-MOKE at iron and cobalt films and self-organized islands on W(110). For recording hysteresis curves an external electromagnet has been applied to the setup. Close to the core levels of e.g., iron and cobalt, the reflectivity and the Kerr rotation is strongly enhanced by resonant forward scattering. We could observe huge intensities in reflexion and intensity asymmetries of 50% at Fe and Co films of less than 6ML. The experimental results will be compared to recent calculations. When annealing Fe(110) films on W(110) a well oriented Fe island structure can be created. Our experimental data clearly show a rotation of the easy axis with respect to thin films which depends on the original coverage before annealing and on the temperature during thermal treatment. In the case of cobalt on W(110) we have investigated the magnetic properties of fcc- and hcp-cobalt films on clean and modified W(110) surfaces. Although the direction of the easy magnetization axis does not change using different cobalt structures, the remanent magnetization and coercive forces have clearly changed.

Microelectromechanical Systems (MEMS)
Room 130 - Session MM+BI+NS+EL+SS-FrM

New Frontiers in MEMS: NEMS and BioMEMS

Moderator: N.E. McGruer, Northeastern University

8:20am **MM+BI+NS+EL+SS-FrM1 Optomechanical Effects in and Properties of Nanomechanical Resonant Structures***, **L. Sekaric**, M. Zalalutdinov, S.W.P. Turner, A.T. Zehnder, J.M. Parpia, H.G. Craighead,* Cornell University

Recently we reported optical excitation and parametric amplification@footnote 1@ of single-crystal silicon MEMS oscillators with resonant frequencies up to 1MHz. Utilizing the interferometric pattern of a laser beam in a Fabry-Pérot cavity formed by the oscillator, we demonstrated a mechanism which can be used both as a driving/amplification scheme and a detection scheme. Here we report observation of this phenomena in single-crystal silicon nanomechanical oscillators with frequencies up to 25MHz and with dimensions up to 2um. High mechanical quality factors (Qs) of these structures were instrumental in enabling us to observe these phenomena. Qs of micron-scale and sub micron structures have been observed to have been relatively low (~ 10@super 3@) as measured in vacuum and at room temperature. We succeeded in improving the Qs of these devices (~ 10@super 4@) at room temperature and high vacuum. We will describe the bulk and surface treatments used to achieve high Q. In addition, these structures act as passive modulators of the laser light at their resonant frequencies. The sensitivity of the measurement technique and the inherent amplification of the motion via the optical drive presents us with a very efficient interferometer/modulator easily integrable on chip. Our initial modeling shows that the laser power needed to set these devices into oscillation is only up to few tens of microwatts. Our long-standing interest in nanomechanical structures fabricated in different materials, presents us with a natural extension for our current and future work - clearly being at an advantage of using this driving scheme even with electrically insulating device layers and with no theoretical frequency limit. @FootnoteText@ @footnote 1@ M. Zalalutdinov, A. Olkhovets, A. Zehnder, B. Ilic, D. Czaplewski, H. G. Craighead, and J. M. Parpia, "Optically pumped paramagnetic amplification for micromechanical oscillators" , Appl. Phys. Lett., Vol. 17 (16) 181 (2001)).

8:40am **MM+BI+NS+EL+SS-FrM2 Micromechanical Cantilever Magnetometers with Integrated Quantum Dots***, **M. Wilde**, M. Schwarz, D. Grundler, C. Heyn, D. Heitmann,* University of Hamburg, Germany

We have prepared highly sensitive micromechanical cantilever magnetometers with integrated semiconductor quantum dots. They allow us to study, for the first time, the very tiny magnetic moment of the quantum dots which contain only a few 100 electrons. We have used GaAs-AlAs-molecular beam epitaxy with its inherent atomic precision, both, for the optimization of the mechanical properties of the cantilever and for the monolithic integration of the investigated electronic nanostructures.@footnote 1@ Using laser-interference lithography, tailored periodic arrays of quantum dots have been prepared on the beam. Experiments have been performed down to a temperature of 250 mK in a magnetic field up to 16 T. Field-induced magnetic oscillations have been observed on the quantum dots. The magnetization is significantly different from that of the two-dimensional reference sample and exhibits several new features. Our results suggest that, both, the quantum confinement and the effect of electron-electron interaction have an important effect on the magnetic moment of the quantum dots. Support by the Deutsche Forschungsgemeinschaft Gemeinschaft via Sonderforschungsbereich SFB 508 is gratefully acknowledged. @FootnoteText@ @footnote 1@ M. Schwarz, D. Grundler, I. Meinel, Ch. Heyn, and D. Heitmann, Appl. Phys. Lett. 76, 3564 (2000).

9:00am **MM+BI+NS+EL+SS-FrM3 Nano-Electromechanical Systems: Physics and Applications***, **R.H. Blick**,* Ludwig Maximilians University, Munich, Germany **INVITED**

Mechanical devices in combination with modern semiconductor electronics offer great advantages as for example their robustness against electrical shocks and ionization due to radiation. The main disadvantage of mechanical devices so far is the low speed of operation. This has been overcome with the realization of nanomechanical systems (NEMS), which allow operation at frequencies up to 500 MHz. I will discuss recent work on such nanomechanical resonators focussing on nonlinear dynamics, mechanical mixing, parametric resonance, and possible uses in quantum squeezing experiments. Furthermore, I will present record mechanical quality factors of Q > 10000. Finally, I will outline an approach to using NEMS for applications in biology (Bio-NEMS).

9:40am **MM+BI+NS+EL+SS-FrM5 Zeptonewton Force Detection at Millikelvin Temperatures***, **H.J. Mamin**, D. Rugar,* IBM Almaden Research Center

Scanning force microscopes routinely operate with forces in the piconewton range, but new applications such as cantilever-based magnetometry and magnetic resonance force microscopy demand force resolutions that can be a million times smaller. The minimum detectable force is ultimately limited by the dissipation in the cantilever and its temperature. We have pushed this limit by cooling a single-crystal silicon cantilever in vacuum to a temperature below 100 mK. To sense the sub-angstrom thermal-mechanical motion with minimal heating of the cantilever, an improved optical fiber interferometer was developed that could be operated at optical powers as low as 2 nW. The cantilever mean square amplitude of vibration showed the expected linear dependence on temperature down to 400 mK, at which point other noise sources became significant. At the lowest temperature, the cantilever achieved a noise temperature of 220 mK, with a corresponding force noise of 820 zeptonewtons in a 1 Hz bandwidth.

10:00am **MM+BI+NS+EL+SS-FrM6 Chemical Detection Based on Nanostructured MEMS Sensors***, **P.G. Datkos**,* Oak Ridge National Laboratory*; M.S. Sepaniak, N. Lavrik, C.A. Tipple,* University of Tennessee

The recent advent of MEMS devices has opened-up new possibilities for chemical detection. Microcantilevers respond to chemical stimuli by undergoing changes in their bending when molecules adsorb on their surface. Increased effective surface area is important in such systems because it results in increased total energy of interfacial interactions. In fact, in nanostructured surfaces (quasi 3-D interfaces) the effective surface stresses can significantly exceed true surface stresses. We used electron beam lithography to fabricate ordered nanofeatures on the surfaces of a microcantilever, We then functionalized the nanostructured surface with a beta-cyclodextrine coating (to impart chemical selectivity) using self-assembled monolayer techniques. We found an increase of two orders of magnitude when nanostructured coatings have been used. We present and discuss our findings on the interactions of functionalized microcantilevers with tetrachloroethylene molecules.

10:20am **MM+BI+NS+EL+SS-FrM7 Biomedical Microsystems for Minimally Invasive Medical Procedures***, **S. Roy**,* The Cleveland Clinic Foundation **INVITED**

Traditional surgery for many medical problems, including gallstones, endometriosis, and various cancers, usually requires long, deep incisions and a lengthy recovery period. Minimally invasive surgery, also known as "keyhole" or "band-aid" surgery, has been used for several years as an alternative to traditional "open" surgery. Minimally invasive procedures for both diagnostics and therapeutics have generated much attention from clinicians, patients, and healthcare administrators for their ability to reduce patient pain, scarring, and hospital stays. Current tools for minimally invasive procedures typically tend to operate as mechanical appendages of the clinician, but with absence to touch-and-feel sensations and only limited vision. The ability of MEMS technology to develop miniature, low-cost, and sophisticated transducers is particularly attractive for the development of smart surgical tools that enhance clinical efficacy. The talk will present an overview of current and upcoming applications of MEMS technology in cardiology, neurology, and orthopedics that are under development at The Cleveland Clinic Foundation and other institutions. Device examples will include pressure sensors, accelerometers, strain gauges, flow meters, valves, pumps, imaging transducers, drug delivery systems, and cutting tools.

11:00am **MM+BI+NS+EL+SS-FrM9 Fabrication Process and Resulting Structures for a Micron-Scale Force-Detected Nuclear Magnetic Resonance (NMR) Spectrometer***, **L.A. Madsen**, G.M. Leskowitz, D.P. Weitekamp,* California Institute of Technology*; W. Tang, T. George, K. Son,* NASA Jet Propulsion Laboratory

NMR is the most widely used method of analysis of chemical structure and dynamics at the millimeter length scale. In order to overcome the inherent poor sensitivity of traditional inductively detected NMR for small samples, we are developing the novel BOOMERANG@footnote 1@ method of force-detected NMR in a homogeneous magnetic field. Our experimental NMR results on liquid and solid 3 mm samples with a prototype spectrometer motivate the scaling of our detectors to observe samples < 100 microns in diameter. Achieving micron-scale detectors will bring about inexpensive NMR spectrometers with superior sensitivity for in-situ analysis, sub-monolayer surface NMR, and massively parallel studies on sample libraries. Ultimately, scaling of these detectors to the nano-scale may allow single-molecule NMR spectroscopy and imaging. We present a microfabrication process for BOOMERANG NMR detectors. This double-sided process utilizes deep RIE to define a Si beam fixed at both ends with a stress buttress at its center. High-aspect ratio NiFe or CoNiFe magnet structures are electrodeposited onto the backside of this beam. A combination of photoresist and oxide sacrificial layers allows ~1 micron spacing between a field compensation magnet and the moving detector magnet, and between the compensation magnet and the Si beam. Initial results of the 6-mask process are promising. We present patterned, electrodeposited magnets on the micro-oscillator substrate, as well as our efforts to characterize the micro-detectors and improve device yield. @FootnoteText@ @footnote 1@ Sol. St. Nucl. Magn. Reson. 11, 73 (1998).

Friday Morning, November 2, 2001

Nanotubes: Science and Applications Topical Conference
Room 133 - Session NT+EL+NS-FrM

Nanotubes: Field Emission

Moderator: T. Yamada, NASA Ames Research Center

8:20am **NT+EL+NS-FrM1 Nanotube Electronic and Transport Properties***, J. Bernholc,* North Carolina State University **INVITED**

Carbon nanotubes can be either metallic or semiconducting. Their properties change significantly with doping and strain, and they are excellent candidates for nanoscale electronic devices and sensors. We have investigated the electronic and quantum transport properties of bent, deformed and tapered nanotubes, as well as nanotube-metal contacts, which will likely form components of future nanotube-based devices. Bent armchair nanotubes keep their metallic character up to fairly high angles, while metallic chiral nanotubes open a sizable gap at the Fermi level, indicating that they can be used as nanoscale strain sensors. Tapered armchair tubes remain metallic, while their zigzag counterparts are semiconducting, as expected. Ballistic transmission is very sensitive to interactions with the substrate and coupling to the contacts. Our ab initio calculations for NT/Al structures show substantial charge transfer and rehybridization effects, which strongly affect the quantum conductance. We have also investigated BN nanotubes that are intrinsically polar. For BN tubes in chiral or zigzag structures, the symmetry permits a pyroelectric field along the tube axis, which is of the order of kV/cm per nanotube. The pyro- and piezo-effects will likely be useful in nanoscale switches, resonators, actuators, and transducers. Another important aspect of nanotubular structures is their high Li uptake, with potential applications in high performance batteries. Our quantum simulations show that Li cannot penetrate nanotube walls unless large defect structures are present, and that high concentration of Li leads to aggregates in the interstitial channels. In collaboration with M. Buongiorno Nardelli, J.-L. Fattebert, V. Meunier, D. Orlikowski, C. Roland and Q. Zhao.

9:00am **NT+EL+NS-FrM3 Laser Irradiation Effect on Field Emission of Carbon Nanotubes***, **T.W. Jeong**, S. Yu, J.H. Lee, J.N. Heo,* Samsung Advanced Institute of Technology, Korea*; W.S. Kim,* Sungkyunkwan University, Korea*; W. Yi,* Samsung Advanced Institute of Technology, Korea*; J.B. Yoo,* Sungkyunkwan University, Korea*; J.M. Kim,* Samsung Advanced Institute of Technology, Korea

Recently, field emission properties of carbon nanotubes (CNTs) have been intensivly studied as electron emission sources in field emission displays, since CNTs exhibit a good emission stability, low operating voltages, and high saturation electric field for field emission. Through current-voltage measurment, we have investigated the effect of laser irradiation on the field emission characteristics of CNT films. Multi-walled CNT thin layers were grown on the Ni/TiN sputtered alumina substrate by thermal chemical vapor deposition (CVD) process, and single-walled CNT layers were fabricated by screen printing of CNT paste onto the glass and subsequent heat treatment. In case of the CNT film grown by the thermal CVD, laser irradiation does not influence the field emission characteristics significantly. On the while, in case of the CNT film prepared by paste process, the field emission current was enhanced up to 10 times after the irradiation. Main reason for the current increase is considered as thermal heating by the laser, since organic materials existing in the paste-processed CNTs are detached out by the heat exposure leading to a clean surface of electron emitting CNTs. When the intensity of the laser was increased over a certain level, the emission current was reduced due to CNT deterioration by the heat. Therefore, laser irradiation onto the paste-processed CNTs is worthwhile for further study since currently available CNT based FEDs are fabricated mainly by paste process.

9:20am **NT+EL+NS-FrM4 Saturated Emission Near E@sub F@ from Multiwall Carbon Nanotubes***, **J.L. Shaw**, D.S.Y. Hsu,* Naval Research Laboratory

Energy distributions of the beam emitted from gated multi-wall carbon nanotube arrays@footnote 1@ are measured in UHV as a function of gate voltage (emission current), temperature, and gas exposure. The emitters were grown by catalyzed CVD on silicon. At low currents (~1nA), the shape of the energy distribution was similar to that of metal emitters. At moderate current, emission could be detected at energies up to several volts below the Fermi level. The spectral shape at lower energies varied among specimens, after degassing, and after exposure to water. The intensity at the lower energies was reduced after degassing and increased by water adsorption. Operating the emitters removed the water at a rate related to the emission current. At increasing voltage, the fraction of the current emitted at the lower energies increased, while the emission current near the Fermi level saturated. That is, the additional current emitted after increasing the gate voltage occurred only below a specific energy, and that specific energy moved further below the Fermi level at higher voltages. The saturation effect was reduced by elevated temperatures (up to 600C) but still dominated the spectra, indicating that transport through the silicon substrate or at the silicon-nanotube interface was not responsible. Instead, we believe the emission at a specific energy is limited by the ability of the nanotube to replace electrons near the Fermi level, leaving only lower energy electrons available for emission. @FootnoteText@ @footnote 1@ D.S.Y Hsu, these proceedings

9:40am **NT+EL+NS-FrM5 Integrally Gated In-situ Grown Carbon Nanotube Field Emitter Arrays***, **D.S.Y. Hsu**, J.L. Shaw,* Naval Research Laboratory

We report on the fabrication of two different configurations of integrally gated carbon nanotube field emitter arrays and the associated field emission. Local control of field emitter arrays, usually by gating, is necessary for most applications. Although several designs of gated carbon nanotube field emitter arrays, all based on a nanotube paste or slurry technology, have been demonstrated, to date no integrally-gated microfabricated carbon nanotube field emitter arrays based on in-situ-grown carbon nanotubes have been reported. We grew carbon nanotubes directly on gated cell structures in a cold-walled hot-filament CVD reactor at 650- 700 C using ammonia and acetylene or ethylene reactant gases and Ni or Fe catalysts. In one configuration, multi-walled carbon nanotubes with 20-30nm average diameter were grown on the tips of standard gated silicon tip-on-post field emitter arrays with 2.5 micron diameter gate apertures. Typical threshold voltages were less than 20V. For a 37 thousand cell array our highest collected anode current to date was 1.1 mA at a gate voltage of 41V. Stable emission even at 600 C has been obtained. Exposure to water vapor shifted the current-voltage curve to lower voltages, consistent with work of Dean and Chalamala@footnote 1@ on ungated single SWNT emitters. We also investigated electron energy distributions under various experimental conditions.@footnote 2@ In a second configuration, we grew multi-walled carbon nanotubes on the bottoms of hole structures with horizontal gate apertures having 1.5 - 2.5 micron diameters. Average emission currents up to 60 nA per cell with anode to gate current ratios greater than 10 have been measured. Economical manufacture of both configurations is projected because the first configuration does not require a sharp tip and the second requires only a much reduced number of steps. @FootnoteText@ @footnote 1@ K.A. Dean and B.R. Chalamala, App. Phys. Lett. 76, 375 (2000). @footnote 2@ J.L. Shaw and D.S.Y. Hsu, this proceedings.

10:00am **NT+EL+NS-FrM6 Field Emission in Cylindrical Geometry with Carbon Nanotube Cathodes: Characterization and Application to Luminescent Tubes***, J.-M. Bonard, M. Croci, O. Noury, T. Stöckli, A. Chatelain,* Ecole Polytechnique Fédérale de Lausanne, Switzerland*; **I. Arfaoui**,* IPE, Switzerland

There have been in the past some attemps to realize tubular lighting elements with field emitters to offer a mercury-free alternative to incandescent or fluorescent lamps. To ensure a uniform light emission from the cylindrical anode, the cathode itself must be cylindrical, and the problem of depositing field emitters on a non-planar surface has up-to-now prevented the demonstration of such devices. We report here on the successful realization of a field emission diode in a cylindrical geometry, with multiwall carbon nanotubes deposited on the metallic cathode as the electron sources. The deposition was carried out by chemical vapor deposition of acetylene over metallic wires, and we observed a significant influence of the wire material. The field emitters show excellent performances: electron emission is observed below 1 kV and currents up to 1 A cm@super -2@ can be obtained. The cathodes can be used to realize luminescent mercury-free tubes: our most recent tube has a length of 30 cm and a diameter of 4 cm, and reaches luminances equivalent to those of commercial fluorescent elements. We show also that the cylindrical geometry allows one to gain information on the different parameters involved in the field emission. Space-charge related problems and the influence of residual gas pressure have been addressed. Field emission microscopy measurements show also that modifications of the structure of the nanotubes can occur during the emission, especially during or following heating. Spectacular observations of the failure of single nanotube emitters also offer direct clues to the degradation mechanism.

10:20am **NT+EL+NS-FrM7 Fabrication and Electron Field Emission Properties of Carbon Nanotube Films by Electrophoretic Deposition***, **G.Z. Yue**, B. Gao, Q. Qiu, Y. Cheng, H. Shimoda, L. Fleming, O. Zhou,* University of North Carolina

Carbon nanotubes have recently attracted considerable interests as electron field emitters for potential vacuum microelectronic applications such as field emission flat panel displays. Compared to the conventional field emitters, they show lower emission threshold fields and enhanced high current capabilities. However, their utilization in practical devices has been hindered, in part, by difficulties in processing. In this paper, we demonstrate that the electrophoretic deposition (EPD) method can be utilized effectively to deposit pre-formed carbon nanotubes on various substrates with good homogeneity and packing density. The films show very good emission stability at high current densities.

10:40am **NT+EL+NS-FrM8 Field Emission Energy Distribution for an Undergate Type Triode CNT-FED***, S.H. Jin, **S. Yu**, J.H. Kang, W. Yi, T.W. Jeong, Y.S. Choi, J.H. Lee, J.N. Heo,* Samsung Advanced Institute of Technology, Korea*; W.S. Kim, Y.H. Lee,* Sungkyunkwan University, Korea*; J.M. Kim,* Samsung Advanced Institute of Technology, Korea

We have measured I-V characteristics and field emission energy distribution (FEED) for an undergate-type triode carbon nanotube (CNT) field emission display (FED), which has gate electrodes located under the cathode electrodes. The emitters of an undergated CNT-FED were fabricated by the printing method on the glass plate with single walled CNT paste, which was mostly consisted of CNTs and glass powders. For the diode emission, the FEED peaks shifted from the Fermi level with the ratio of 67 meV/V by the change of the applied voltage, and the field enhancement factor was found to be 26,000 cm@super-1@ from the I-V measurement. On the while, the peaks for the triode emission shift with 270 ~ 500 meV/V, and it is expected mainly due to the strong electric field induced by the gate electrodes. Several subpeaks were also observed below the main FEED peaks, which indicated existence of other minor electron transition mechanism within CNTs. The full width at half maximum of FEED peaks for the diode and triode emissions were broader than those reported by others, i.e., 0.7 ~ 1.9 eV, which may be caused by field emission from various geometry of CNTs. In summary, we have measured the FEED of the undergate type triode CNT-FED for the first time, and the FEED peaks are shifted as the applied voltage increased, which may be ascribed to the energy band bending of dielectric materials on CNTs.

11:00am **NT+EL+NS-FrM9 Integrated Field Emission Devices with Single Carbon Nanofiber Cathodes***, **M.A. Guillorn**, V.I. Merkulov,* Oak Ridge National Laboratory*; A.V. Melechko, E.D. Ellis,* University of Tennessee*; G.J. Bordonaro,* Cornell University*; L.R. Baylor, J.H. Whealton, M.L. Simpson, D.H. Lowndes,* Oak Ridge National Laboratory

The fabrication of robust integrated field emission (FE) devices is currently an area of intense research. FE devices require an electron source with a low threshold field and stable operating characteristics. Recently, we have focused on vertically aligned carbon nanofibers (VACNFs)@footnote 1@ as FE sources for these reasons.@footnote 2@ In this paper we will present field emission data on isolated VACNFs measured by a scanned probe technique and device performance of integrated gated cathode and triode structures that use a single VACNF as the FE element. Isolated high aspect ratio VACNFs were grown on Si substrates using a DC acetylene/ammonia PECVD process from catalyst sites defined with electron beam lithography (EBL). FE properties of individual VACNFs were measured with a scanned probe system capable of positioning a 1-micron diameter probe tip above an individual VACNF. Gated cathode and triode structures using individual VACNFs as FE elements were fabricated using a combination of traditional micro- and nanofabrication techniques.@footnote 3@ EBL was used to define the first layer of features consisting of catalyst sites for VACNF growth and alignment marks for subsequent photolithography steps. Alternating layers of PECVD silicon dioxide and metal were then deposited onto the substrate and patterned using photolithography creating electrostatic extractor and focus electrodes aligned with the catalyst site. The dielectric layers were reactive ion etched until the buried catalyst sites were released. To complete the devices the growth of the VACNF was performed as described above. The FE current from these devices was measured using a micro channel plate system. @FootnoteText@ @footnote 1@V.I. Merkulov, D.H. Lowndes, Y.Y. Wei, G. Eres, E. Voelkl, Appl. Phys. Lett., 76, 3555 (1999) @footnote 2@V.I. Merkulov, D.H. Lowndes, L.R. Baylor, J. Appl. Phys, 89, 1933 (2001) @footnote 3@M.A. Guillorn, V.I. Merkulov, G.J. Bordonaro, et al, J. Vac. Sci and Tech. B, 19, 573 (2001).

11:20am **NT+EL+NS-FrM10 Advances in Conception of Flat Panel Displays Based on Carbon Nanotube Field Emitters***, **I. Arfaoui**, J.-M. Bonard,* EPFL, Switzerland*; D. Sarangi,* EPFL, Switzerland, France*; J. Dijon,* CEA, France*; A. Chatelain,* EPFL, Switzerland

Because of their unusual sharpness and conducting properties, Carbon NanoTubes (CNT) are an ideal candidate material for field emitting tips. In order to develop a technology allowing the fabrication of low cost large area Field Emission Displays (15 - 40), we therefore used CNT as field emissive materials. For that, it is important to have an optimised deposition method of well-aligned and well-distributed carbon nanotubes on large area substrate at low or moderate temperature. Our work deals with the growth and FE properties of CNT films on Si substrates. These patterned emitting films are made by Chemical Vapour Deposition: the CNT grow preferentially on Si substrates where a metallic catalyst (i.e. Ni, Co, Fe...) is deposited by sputtering followed by standard lithography, by microcontact printing or ink jet printing. We have optimised growth parameters (catalyst, temperature, ...) in order to obtain the lowest threshold emission fields and the highest emitting site density. However, we have shown that emitting site density is the most important parameter for Flat Panel Displays. Two particular points are discussed: structural and FE properties of diode and triode structures and a model of the emission process. In order to improve the cost issue as well as the reliability of FED, we have studied innovative triode structures. Finally, a microscopic model of the emission process is used to predict emission life and spatial uniformity of CNT films.

11:40am **NT+EL+NS-FrM11 Huge Secondary Electron Emission from Coated Carbon Nanotubes***, **J.N. Heo**,* Samsung Advanced Institute of Technology, Korea*; W.S. Kim,* Sungkyunkwan University, Korea*; T.W. Jeong,* Samsung Advanced Institute of Technology, Korea*; Y.M. Shin, H.J. Jeong,* Sungkyunkwan University, Korea*; S. Yu, J.H. Lee, W. Yi,* Samsung Advanced Institute of Technology, Korea*; Y.H. Lee,* Sungkyunkwan University, Korea*; J.M. Kim,* Samsung Advanced Institute of Technology, Korea

Carbon nanotubes (CNTs) have been reported to show very attractive properties such as high geometric anisotropy, high mechanical strength, and chemical stability, which leads to potential applications in the areas of display, nanoelectronics, and nano-sensors. According to the recent report by W.Yi and et al.(J. Appl. Phy. 89, 4091(2001)), huge secondary electron emission (SEE), i.e., value higher than 10@super 4@, was obtained for the MgO coated CNTs. In order to understand this high SEE feature systematically, a seres of samples have been fabricated by varying several parameters such as the thickness of the MgO layer, openness of the CNT tip, selectively growing of CNTs on patterned catalytic layer. CNTs were grown vertically by a thermal chemical vapor evaporator on the Si substrates with Ni and TiN thin layer. MgO or other dielectric layers were deposited on CNTs by an electron beam evaporator. Among the sample grown parameters, especially MgO thickness variation resulted in significant SEE yield change. From the thickness variation of coated CNTs from 60 to 450 nm, the maximum SEE yield was obtained for 150nm. From the energy distribution of secondary electrons, this huge SEE yield for a coated CNT is illustrated with the help of field enhanced SEE due to high geometrical aspect ratio. In addition, experimental results for different dielectric layers such as SiO@sub 2@ or LaF@sub 3@ will also be presented.

Plasma Science

Room 104 - Session PS-FrM

Diagnostics III

Moderator: M.C.M. van de Sanden, Eindhoven University of Technology, The Netherlands

8:20am **PS-FrM1 Optical Diagnostics of Charged Particles in Processing Plasmas***, **A. Kono**,* Nagoya University, Japan **INVITED**

Behaviors of electrons and negative ions in low-pressure high-density inductively coupled plasmas have been studied using non-intrusive optical diagnostic techniques. An efficient multichannel laser Thomson scattering measurement system, which is highly resistant to Rayleigh scattering interference, was developed and used to study electron energy distribution functions (EEDFs). In measurements of C@sub 4@F@sub 8@/Ar plasma at a total pressure of 25 mTorr, non-Maxwellian EEDFs were observed, in contrast to Maxwellian EEDF observed for pure Ar plasma. A particle simulation suggests that the observed EEDFs result from local electron heating and subsequent cooling of electrons by inelastic collisions in the non-heating region. Laser photodetachment technique in combination with millimeter-wave Fabry-Perot resonance technique was used to study negative ion density. Measurements of CF@sub 4@/, C@sub 4@F@sub 8@/, SF@sub 6@/, and NF@sub 3@/Ar plasmas at 25 mTorr show that at an Ar dilution ratio as high as 95% and at electron densities around 10@super 11@ cm@super -3@, the negative ion density is higher than or nearly as high as the electron density. This indicates that in high-density C@sub 4@F@sub 8@, SF@sub 6@, and NF@sub 3@ plasmas electron attachment occurs as effectively as in low-density plasmas with low dissociation degrees of the feedstock gases; on the other hand, in high-density CF@sub 4@ plasma, electron attachment takes place much more effectively than in low-density plasma, suggesting that dissociation of CF@sub 4@ results in production of highly electron-attaching species.

9:00am **PS-FrM3 Measurements of the Spatiotemporal Variation of Ion Flux in Plasma Etching Reactors***, **T.-W. Kim**, S.J. Ullal, E.S. Aydil,* University of California, Santa Barbara

Variation of the ion flux and its spatial distribution across the wafer is critical in plasma etching: ion flux uniformity at the wafer determines the uniformity of etching. Most ion flux uniformity measurements to date have concentrated on studying the radial uniformity on a plane above the wafer. There are very few ion flux measurements on the plane of the wafer, especially in two dimensions. We have designed, built, and used planar Langmuir probes and probe arrays consisting of 10-30 probes on 75 mm and 200 mm diameter wafers to measure the variation of ion bombardment flux and its spatiotemporal distribution at the plane of the wafer in two different inductively coupled plasma reactors. Two-dimensional variation of the ion flux as a function of radial and angular positions on the plane of the wafer was mapped by interpolating between the probes. We demonstrate the uitility of these probes in studying factors that affect the ion flux and its uniformity including instabilities in an Ar discharge and effects of etching products in Cl@sub 2@ etching of Si. For example, in one of the reactors in Ar plasma at high pressure, a region of high ion flux ("hot spot") developes at the edge of the wafer at seemingly random positions and this "hot spot" rotates and moves around the edge on a time scale that depends on the plasma conditions. During etching of Si in a chlorine plasma, ion flux increases as a function of exposure time to the chlorine discharge and saturates on a time scale that is on the order of a few minutes. Through other diagnostic methods, this reproducible transient in the ion flux is related to the release of etching reaction products such as SiCl@sub x@ and subsequent deposition of a silicon oxychloride film on the reactor walls. Removal of this film from the wall with an SF@sub 6@ discharge resets the reactor walls back to a reproducible condition and returns the ion flux to the same level as at the beginning of the etching process.

9:20am **PS-FrM4 Time-resolved Radical Measurements in a Remote Silane Plasma Using the Cavity Ringdown Absorption Technique***, **J.P.M. Hoefnagels**, A.E.E. Stevens,* Eindhoven University of Technology, The Netherlands*; W.M.M. Kessels, D.C. Schram,* Eindhoven University of Technology, The Netherlands, Netherlands*; M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands

The highly sensitive cavity ringdown spectroscopy technique (CRDS) has been used for the determination of the density and plasma chemistry of SiH@sub x@ radicals in our remote silane plasma, which is used for high rate deposition of a-Si:H and µc-Si:H. Recently, a new CRDS based technique has been developed for measuring time-resolved radical densities (@tau@-CRDS) to obtain further insight into the dynamics of SiH@sub x@ radicals and to study the interaction of these radicals with the depositing surface. In @tau@-CRDS, the plasma is modulated and the corresponding response of the SiH@sub x@ radical density is monitored by sampling the SiH@sub x@ density at various times. For this measurement, a "state of the art" data acquisition system (100 MHz, 12 bit) has been developed such that single CRDS transients can be handled up to a repetition rate of 2 kHz. It will be shown that single transient handling improves the signal-to-noise ratio drastically, even for conventional CRDS measurements. The modulation of the plasma is done by application of pulsed rf power to the substrate holder in addition to the regularly operating remote plasma. This creates only a minor additional SiH@sub x@ radical density. In this way, gas phase and surface reactivities of the species are obtained under steady state plasma operation conditions. The feasibility of the @tau@-CRDS technique has been proven on SiH radicals probing the A@super 2@@DELTA@<-X@super 2@@PI@ electronic transition at ~413 nm. By using different modulation frequencies the measurements have also revealed that a previously unidentified broadband absorption on this wavelength is due to a rather unreactive species created in the silane plasma. Furthermore, @tau@-CRDS measurements on Si and SiH@sub 3@ will be presented and the gas phase and surface reactivity of these species will be discussed on the basis of a model.

9:40am **PS-FrM5 Temporally Resolved Measurement of Electron Temperature, Relative Electron Density, and Atomic Fluorine Density during Fluorocarbon/Rare-gas Plasma Etching of SiO@sub 2@, using Optical Emission Spectroscopy***, **M.J. Schabel**,* Bell Laboratories, Lucent Technologies*; V.M. Donnelly, W.W. Tai, A. Kornblit,* Agere Systems

Measuring the time-resolved behavior of processing plasmas is important for determining process end-points, tool health and process faults. One commonly used approach is to monitor the optical emission for changes that correlate conditions. Recently, we have demonstrated that the plasma emission may also be used to characterize the time-averaged behavior of fundamental plasma properties, including electron temperature (T@sub e@), relative electron density (n@sub e@) and fluorine atom concentration (n@sub F@), through the application of advanced optical emission spectroscopy. Here we have used trace rare gas optical emission spectroscopy and rare gas actinometry to measure T@sub e@, n@sub e@, and n@sub F@ at ~2 second increments in an inductively-coupled commercial plasma reactor. The temporal behavior was evaluated over a complete plasma process cycle, which included plasma strike, stabilization, chamber seasoning, silicon dioxide etch, and an oxygen chamber clean and photoresist strip. Run to run repeatability of T@sub e@, n@sub e@, n@sub F@, and O-atom density was evaluated for each step in the cycle. T@sub e@ was found to be repeatable to within ± 0.5 eV for constant step conditions. The silicon dioxide etch step, comprised of C@sub 2@F@sub 6@, C@sub 4@F@sub 8@, a carrier gas, and a trace rare gas mixture (equal parts He, Ne, Ar, Kr, and Xe), was evaluated over variations in pressure (10-90 mTorr), flowrate (120-600 sccm), and carrier gas composition (0-100% Ar, balance Ne). Corresponding measurements of etch rates and sidewall angles were found to range between 2-12 kÅ/min and 85-90°, respectively. Correlations between plasma operating conditions, fundamental plasma parameters, and etch performance will be presented.

10:00am **PS-FrM6 Characterization of Mass-Filtered CF@sub x@@super +@ Ion Beams for Surface Studies of Etching***, **M.J. Gordon**,* California Institute of Technology*; K.P. Giapis,* California Institute of Technology, U. S. A.

Many ion beam systems used to probe plasma-surface interactions during etching are unable to deliver the tunable energy and high particle flux conditions that are typical of realistic processing plasmas. Some of the problems include inefficient ion production, space charge spreading of the beam resulting in very low fluxes, and a fixed plasma potential that requires the sample to be offset from ground in order to vary the beam energy. Furthermore, mass-filtering of the ion beam is required if the reaction dynamics of specific plasma species are to be understood. To create an improved ion source for etching studies, we have developed a mass-filtered ion beam system based on extraction of ions from an inductively coupled plasma (ICP) discharge. In our system, ions are extracted from an ICP discharge (13.56 MHz) using an accel-decel lens arrangement and injected into a transport line floating at -15 kV. The ion beam is mass filtered at high voltage using a magnetic sector, focused, and then decelerated to impinge on a grounded sample. Similar to biasing a wafer, capacitively coupled RF (15-30 MHz) from an auxiliary electrode is used to vary the ICP plasma potential and hence, vary the ion beam energy. Mass-filtered ion currents after focusing that approach 1 mA/cm@super 2@ can be obtained due to high ion densities in the ICP and beam transport at high voltage to avoid space charge spreading. This talk will focus on ion source design and beam characterization experiments for CF@sub x@@super +@ species extracted from ICP etching plasmas. The dependence of CF@sub 2@@super +@/CF@sub 3@@super +@ beam currents and ion energy distribution functions (IEDF's) on plasma pressure (1-10 mT) and RF inductive power (50-500W) were measured using a hemispherical energy analyzer located downstream of the sector magnet. In addition, the effect of capacitive RF bias power and frequency (15-30 MHz) on the plasma potential was investigated by monitoring the shift in the beam IEDF.

10:20am **PS-FrM7 Ion Energy Measurements in a Pulsed Plasma with a High-resolution, Submicron, Retarding Field Analyzer***, **M.G. Blain**, M.J. Sowa, R.L. Jarecki,* Sandia National Laboratories

A silicon wafer-based, submicron, high-resolution, retarding field analyzer (RFA)@footnote 1@ was used to measure ion energy distributions in an inductively coupled plasma where the source power was pulsed on and off. Experiments were conducted in argon at pressures from 1.5 - 40 mTorr, with various source rf powers, for periods of 10-40 µsec with duty factors from 20%-80%. In contrast to the single peak obtained with continuous Ar plasmas, distinct high and low ion energy peaks were frequently observable in the pulsed plasmas. These distinct peaks can be attributed to contributions from a high T@sub e@ inductively-powered plasma, and a low T@sub e@ afterglow, respectively. A simulation based on the global plasma model of Ashida, et al.@footnote 2@ was able to capture the qualitative trends in the pulsed data, confirming this interpretation. Additional pulsed experiments were performed with 0-100% O@sub 2@/Ar mixtures, as well as various Cl@sub 2@/Ar mixtures. Oxygen addition, in particular, produces an increased spread between the high and low energy peaks, perhaps due to depletion of electron density by attachment during the afterglow.@footnote 3@ @FootnoteText@ @footnote 1@M.G. Blain, J.E. Stevens, J.R. Woodworth, Appl. Phys. Lett., v.75, n.25, p.3923, 1999. @footnote 2@S. Ashida, C. Lee, and M. A. Lieberman, J. Vac. Sci. Technol. A, v.13, n.5, p.2498, 1995. @footnote 3@Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

11:00am **PS-FrM9 Characteristics of the LAPPS Ion Flux to an RF Biased Surface***, **D.D. Blackwell**, S.G. Walton, D. Leonhardt, D.P. Murphy, R.F. Fernsler, R.A. Meger,* US Naval Research Laboratory

The ion flux properties are possibly the most critical parameters in a process plasma. Every industrial plasma process, from sputtering to deposition, is highly dependent on the density, energy, and composition of the ions. At NRL, we have been experimenting with electron-beam produced plasmas as an alternative to radiofrequency (RF) driven discharges. The most promising of these sources is the hollow cathode driven Large Area Plasma Processing System. This source is designed to produce large area (> 1 m@super 2@), high density, uniform sheets of plasma. In this presentation we will show measurements of the ion energy distribution function (IEDF) from continuous and pulsed electron beam plasmas produced in 20-30 wide, 1 cm thick sheets by a 2 kV hollow cathode. The IEDF is obtained using a gridded energy analyzer incorporated into a RF biasable stage. The surface flux and IEDF in the presence of large RF voltages applied to the stage will be presented. We will also be comparing the IEDF's taken in a pulsed system and a continuous current system during the "beam on" and afterglow periods to observe their temporal evolution. Typical operating conditions are 15-20 millitorr of argon, oxygen, or nitrogen, and 150-200 Gauss magnetic field.

Semiconductors
Room 111 - Session SC+SS-FrM
Growth and Epitaxy of Semiconductors

Moderator: A.A. Baski, Virginia Commonwealth University

8:40am **SC+SS-FrM2 STM Observations of the Initial Growth Process of Ge on Si(105) Surfaces: the Stability of Ge/Si(105) Surfaces***, **Y. Fujikawa**,* University of Wisconsin-Madison*; T. Sakurai,* Tohoku University, Japan*; M.G. Lagally,* University of Wisconsin-Madison

The mechanism of the formation of self-organized SiGe quantum dots on the Si(100) surface has been intensively investigated because of the technological importance of achieving uniform size and high order in the dots. Although it has been demonstrated that the strain created by the lattice mismatch between Ge and Si plays an important role in the transition to 3D island growth and in 3D island ordering, there still is no satisfactory explanation of SiGe(105) facet formation, which creates the regular shape of the SiGe islands. We have used STM to observe the surface structures formed when Ge is deposited on Si(105) surfaces, in order to clarify the coverage dependence of the stability of the (105) surface. When the Ge coverage is greater than 0.5 ML, a p(2x1) reconstructed stable surface is observed, as previously reported.@footnote 1@ At a coverage of ~ 0.5 ML or less, we observe formation of a p(4x1) structure over parts of the surface. The transformation to a p(4x1) structure is complete at 0.04 ML coverage. Decreasing the Ge coverage to 0.02 ML results in roughening of the Si(105) surface. During the transition from the p(2x1) to the p(4x1) structure, a significant change in surface morphology is observed. At coverages of 0.2 ML or less, the formation of the topmost layer tends to start from upper-step edges, while it starts from lower-step edges for coverages above 0.2 ML. As a result, defect arrays are frequently observed at the lower-step edges when the coverage is 0.2 ML or less, due to the incomplete formation of the topmost layer at the lower-step edges. This result clearly indicates the presence of increased strain on the Ge/Si(105) surface as the coverage of Ge is reduced. Ge thus stabilizes the surface. This work is partially supported by NSF and by the Ministry of Education, Culture, Sports, Science and Technology, Japan. @FootnoteText@ @footnote 1@ Tomitori et al., Surf. Sci. 301 (1994) 214.

9:00am **SC+SS-FrM3 Modulated Semiconductor Structures Studied by In Situ Scanning Tunneling Microscopy***, **C.A. Pearson**, C. Dorin, Y. Chen, J. Mirecki Millunchick, B.G. Orr,* University of Michigan-Flint

Semiconductor structures known to exhibit compositional modulation are compared to similar structures that do not exhibit compositional modulation using in situ scanning tunneling microscopy. The structures are grown by molecular beam epitaxy on InP(001) following the growth of a lattice matched InGaAs buffer layer. InAs/GaAs and InAs/AlAs short period superlattices (SPSs) can be classified as having either rough or smooth interfaces. Rough interface SPSs exhibit compositional modulation. The buffer layer and smooth interface SPSs are structures that do not exhibit compositional modulation. Images of these structures are characterized by long wavelength surface undulations. This contrasts significantly from images of modulated structures, which show both long and short wavelength surface undulations. Another distinction is that the lattice planes on the modulated structures appear much more dendritic due to the short wavelength undulations. The relationship between the morphology of the buffer layer and the resulting SPS structure is discerned through these comparisons. Segregation of species is identified as well using scanning tunneling spectroscopy. Results from proximal probe experiments will increase the atomistic understanding of surface roughness and its role in compositional modulation.

9:20am **SC+SS-FrM4 Scandium Gallium Nitride Alloys and ScN/GaN Heterostructures Grown by Molecular Beam Epitaxy***, **A.R. Smith**, H.A.H. Al-Brithen, D.C. Ingram,* Ohio University

Scandium nitride is an interesting transitional metal nitride semiconductor with a simple crystal structure (rocksalt). Part of the interest in ScN is as a lower bandgap material (Eg = 2.1 eV) which can be combined with GaN to form novel heterostructures or alloys. In particular, GaN has a lattice constant close to ScN (both about 4.5Å); it may therefore be possible to form an alloy with band gap in the range 2.1-3.4 eV. However, since ScN is rocksalt while GaN is zincblende or wurtzite, it is not clear that a simple alloy or interface can be formed. We have first investigated the growth of pure ScN on magnesium oxide (001) substrates by molecular beam epitaxy (MBE) using a RF-plasma source and a scandium effusion cell. The Sc/N flux ratio was found to be critical in determining the structural, optical, and electronic properties of the grown epitaxial layers. Under N-rich conditions, the growth is epitaxial, and we find atomically smooth terraces separated by steps having height a/2. Films grown N-rich are stoichiometric and transparent with a direct optical transition at 2.15 eV; further efforts are underway to experimentally verify the theoretically predicted indirect transition near 1 eV. We have begun to investigate the growth of GaN/ScN(001). First, we grew ScN(001) at growth temperature 850°C; next, we initiated GaN growth at reduced substrate temperature 550°C under Ga-rich conditions. After several minutes, the growth temperature was increased to 750°C, and the Ga flux was reduced but still maintaining Ga rich conditions. Reflection High Energy Electron Diffraction (RHEED) showed a pattern consistent with cubic GaN(001). X-ray diffraction showed only one peak beside the MgO substrate peak revealing that the GaN film is cubic having the same (002) orientation as the ScN(001) layer. A Sc-Ga-N layer was also grown on MgO(001) with growth temperature at 850°C. Structural and optical properties will be presented.

9:40am **SC+SS-FrM5 Formation and Decay Processes of Silicon Mounds on Si(111) Surfaces***, **A. Ichimiya**, K. Hayashi,* Nagoya University, Japan*; E.D. Williams, T.L. Einstein,* University of Maryland*; M. Uwaha,* Nagoya University, Japan **INVITED**

Two types of isolated single silicon pyramids on the Si(111) surfaces between 700K and 800K have been produced using an STM tip. Pyramids of 75% are normal stacking at the interface between the pyramid and the substrate (called type U). For pyramids of 25% which are in the twin relation of the type U pyramids, there is a stacking fault at the interface (called type F). The pyramids have certain facets just after the creation. Indices of main facets of the mounds on the Si(111) surface are {311}, and small facets are {221} for the type U and {331} for the type F. Just after the production, the pyramid begins to decompose. During the decay of the type U pyramid, the facets of the pyramid transform into multi-bilayer steps. Finally the mound becomes a bilayer mound (2D) with a truncated triangle shape. The longer edges of the 2D mounds are along the unfaulted halves of the DAS structure of the substrate, while these edges are the shorter one of the pyramid. The decay process of the type F pyramid is layer-by-layer without step bunching. Decay rates of the type F pyramids are about 3 times larger than those of the type U due to the stacking. The energy state of the type F pyramids is about 0.06eV higher than that of the type U. We have measured height evolution of the pyramids during decay, and found that the height decay is due to the power law , t@super 1/4@, where t is the decay time. Such the simple law is predicted by Israeli and Kandel@footnote 1@ for infinite cone decay. It should be noted that such the simple law is in very good agreement with the experimental results of silicon pyramid decay. The results are explained by attachment-detachment limited processes at step edges. The measured decay rates are in very good agreement with decay rates which are evaluated from those of 2D mounds.@footnote 2@ @FootnoteText@ @footnote 1@ N. Israeli and D. Kandel, Phys. Rev. Lett. 80, 556 (1998. @footnote 2@ A. Ichimiya, Y. Tanaka and K. Ishiyama, Phys. Rev. Lett. 76, 4721 (1996).

10:20am **SC+SS-FrM7 Role of Surface Steps in the Arrangement of Silicon Nano-dots on Vicinal Si(111) Surfaces: STM Investigation*, J.S. Ha,*** *K.-H. Park, Y.-J. Ko, K. Park,* ETRI, Republic of Korea

Regular array of nano-structures such as dots and wires can be obtained by elaborate control of chemical reactions on stepped surfaces. In this work, we have investigated the role of surface steps in the arrangement of silicon nano-dots on vicinal Si(111) surfaces by scanning tunneling microscopy(STM). Nanometer sized silicon nitride islands were formed on a vicinal Si(111) surface, which was 1@super o@ off toward [112] direction, via thermal nitridation using N@sub 2@ gas. On the nitrided surface, oxygen gas was dosed at 700 @super o@C to induce a local selective etching of silicon using silicon nitride islands as masks. The resultant surface showed one-dimensional arrangement of silicon nano-dots along the step edges of the silicon surface. The lateral size of the dot in the direction perpendicular to the step edges was restricted to the terrace width of the stepped Si(111) surface. Preferential growth of silicon nitride islands on the edges of single height steps is considered to be responsible for the arrangement of silicon nano-dots along the step edges of the 1 @super o@ off vicinal Si(111) surface. Furthermore, comparative STM studies to investigate the role of surface steps, which were done on Si(111) surfaces with miscut angles of 0.1@super o@ and 4@super o@ off toward [110] direction, will be also discussed.

10:40am **SC+SS-FrM8 Thermal Growth of High-density Silicon Quantum Dots on SiO@sub 2@/Si(001) with Submonolayer Silicon Adatom Predeposition*, J.G. Ekerdt,*** *J.H. Zhu, W.T. Leach,* University of Texas at Austin

A nonthermal method to facilitate nucleation and subsequent thermal chemical vapor deposition of Si quantum dots on SiO@sub 2@/Si(100) with high density and uniform size is demonstrated. Submonolayers (0.12 to 0.02 ML) of Si adatoms are predeposited on a room temperature to 825 K SiO@sub 2@/Si(001) substrate by cracking disilane on a high-temperature filament in a UHV chamber at pressures on the order of 10@super -7@ Torr. The quantum dots are grown at 825 K with a disilane pressure of 2x10@super -6@super Torr. The Si quantum dot density is increased and size distribution is narrowed by predeposition of Si adatoms when compared to thermal growth on bare SiO@sub 2@/Si(100). The dot density and size is controlled by the amount of Si adatom predeposition; 9.5x10@super 11@ cm@super -2@ density and 5.5 nm size are demonstrated on SiO@sub 2@/Si(001). A surface kinetic model is also presented that accounts for dot nucleation, adatom formation during growth, diffusion of adatoms to growing dots and epitaxial growth of dots. The method provides an effective way to control the nucleation, and consequently the growth, of quantum dots on dielectric surfaces.

11:00am **SC+SS-FrM9 Nucleationless Island Formation in SiGe/Si(100) Heteroepitaxy*, P. Zahl,*** *P.W. Sutter,* Colorado School of Mines

The self-assembly of quantum dot (QD) islands in lattice-mismatched heteroepitaxy has been studied extensively. One of the objectives of recent research is the creation of long-range ordered arrays of QDs of uniform size, a major technological milestone that would pave the way for application of these nanostructures in electronic and optoelectronic devices. The formation of epitaxial QD islands is generally assumed to involve nucleation, a statistical process that would severely impede QD organization. Our recent observations by low-energy electron microscopy, however, have demonstrated that QD islands in heteroepitaxial systems such as SiGe/Si(100) can self-assemble in a coninuous process that avoids nucleation.@footnote 1@ With the observed nucleationless islanding, perfect periodic arrays of uniform QD islands may form spontaneously under suitable growth conditions or may be induced by weakly invasive growth modifiers that enhance existing ordering forces. We present a systematic study of the evolution of SiGe QD islands on Si(100) by combining growth with in-situ scanning tunneling microscopy. Our microscopic observations are analyzed to detect island interaction mechanisms that may act as driving forces for spontaneous spatial ordering in the nucleationless islanding process. First results on the use of growth modifiers to enhance or induce long-range order will be presented. @FootnoteText@ @footnote 1@ P. Sutter and M. G. Lagally; Phys. Rev. Lett., 84(20):4637-4640, 2000.

11:20am **SC+SS-FrM10 Electronic Structure of a Heteroepitaxially-Passivated Si(111) Surface: GaSe-terminated Si(111)*, M.A. Olmstead,*** University of Washington*; R. Rudolf, C. Pettenkofer,* Hahn-Meitner Inst., Germany*; A.A. Bostwick, J.A. Adams,* University of Washington*; E. Rotenberg,* Advanced Light Source, Berkeley*; F.S. Ohuchi,* University of Washington*; R. Fritsche, A. Klein, W. Jaegermann,* Tech. Univ. Darmstadt, Germany

Dissimilar materials heteroepitaxy often results in an interface reaction that passivates substrate dangling bonds. This forms a low energy surface that promotes islanded, rather than laminar, growth of the subsequent overlayer. GaSe-terminated Si(111) is an example of such a stable, low-diffusion barrier surface with no states in the Si band gap; it may serve as an ideal substrate for quantum dot growth on Si(111). We have performed detailed studies of the electronic and atomic structure of GaSe-terminated S i(111) using energy-dependent and angle-resolved valence band and core-level photoemission spectroscopy. The surface termination consists of a Ga layer bonded to the top-most Si atoms and a Se layer on top with each Se atom bonded to three Ga. Our photoelectron diffraction results show the Ga and Se atomic arrangement is identical to that of a half-sheet of the layered semiconductor GaSe. The surface thus contains no dangling bonds, but has fully-occupied lone-pair states similar to As-terminated Si(111). The observed dispersion of the energy bands is very close to those of a GaSe single crystal and is interpreted in terms of tight binding energy states. The dominance of the GaSe-derived states over those of Si-derived states is obvious and is different from As-terminated Si.

11:40am **SC+SS-FrM11 Surface Reaction Study of TaN Growth from MOCVD Precursors on Cu(111)**, *J.-B. Wu,* National Chiao-Tung University, Taiwan*;* ***Y.W. Yang,*** Synchrotron Radiation Research Center, Taiwan*; Y.-F. Lin, H.-T. Chiu,* National Chiao-Tung University, Taiwan

Understanding the reaction pathway followed by MOCVD precursors during thin film growth is a scientifically challenging problem. Transition metal nitride films, due to their wide applications in semiconductor processing, e.g., in areas like diffusion barrier materials, have been extensively studied. However, the knowledge about detailed surface nitride chemistry has been relatively scarce. Here, we report on surface reaction studies of TaN CVD precursors carried out by using high-resolution XPS, TDS, and NEXAFS techniques. The precursors studied include some custom-synthesized compounds (@supert@BuN)Ta(NEt@sub2@)@sub3@ and (@supert@BuN)Ta(NEtMe)@sub3@ that are characterized by the presence of absence of @beta@-methyl groups and by whether singly or doubly-bonded nitrogen being attached to a Ta atom. The @beta@-methyl group is known to influence the decomposition pathway of amido group, which in turn can determine the amount of carbon being incorporated into the films. XPS data show that the formation of nitride species starts at surface temperatures higher than 500 K and, as the reaction proceeds, graphic carbons are incorporated into TaN species and significant Ta oxides are formed due to favorable exothermicity. During the course of surface decomposition, multimass TDS data point to the evolution of hydrogen, hydrocarbon species, and possibly acetonitrile. Oxidation resistance and degree of carbon incorporation are found to vary with the precursors. Based on these results, possible reaction mechanisms and the effect of precursor are to be discussed.

Surface Science
Room 120 - Session SS1-FrM
Dynamics of Metal Surfaces

Moderator: N.C. Bartelt, Sandia National Laboratories

8:20am **SS1-FrM1 Crossover from Surface- to Bulk-Diffusion-Limited Surface Dynamics on Pt(111)@footnote 1@***, B. Poelsema,* University of Twente, The Netherlands*; J.B. Hannon,* IBM T.J. Watson Research Center*; N.C. Bartelt,* ***G.L. Kellogg,*** Sandia National Laboratories

Microscopic measurements of changes in surface morphology due to the motion of single-atom high steps provide detailed information on atomistic processes occurring at a crystal surface. In this study, we use low energy electron microscopy (LEEM) to measure the time-dependent changes in area of two-dimensional Pt islands on Pt(111) as a function of temperature. We find evidence for a crossover from step motion caused by surface diffusion to step motion caused by the flow of material to and from the bulk crystal as the temperature is raised. At temperatures in the range from 1100-1500 K, circular islands residing at the top of three-dimensional stacks exhibit a linear decay, as long as the stack diameter exceeds approximately 1.5 microns. The temperature dependence of the decay rate yields an activation energy of 1.7 eV. On the other hand, for stacks with smaller diameters and temperatures below 1350 K, the decay is non-linear, having a form more closely resembling surface diffusion-limited kinetics. The high-T behavior is similar to that recently observed for NiAl(110), where it was shown that bulk vacancy transport controls step motion on the surface.@footnote 2@ In support of the same interpretation for Pt(111), we observe that the islands grow upon increasing the temperature and shrink upon lowering the temperature in non-equilibrium experiments. The dynamics for Pt(111) are more complicated than NiAl(110), involving a competition between the diffusion of surface adatoms and bulk vacancies. However, preliminary modeling studies indicate that processes involving bulk vacancies can simultaneously explain the temperature dependence of island decay at fixed temperature and the non-equilibrium behavior of islands on Pt(111) as the temperature is varied. @FootnoteText@ @footnote 1@Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U. S. DOE under Contract DE-AC04-94AL85000. @footnote 2@ K. McCarty, J.A. Nobel, and N.C. Bartelt, preprint.

8:40am **SS1-FrM2 Dimensionality Investigation of an Alloy-dealloy Phase Transition on Ag/Cu(110)***, O. Kizilkaya, D.A. Hite, J. Choi,* ***P.T. Sprunger,*** Louisiana State University

An alloy-dealloy phase transition as a result of 0.4-1 ML deposition of Ag on Cu(110) has been studied by use of angle resolved photoemission spectroscopy (ARUPS). The ARUPS measurements were performed at 3m. TGM beamline at Center for Advanced Microstructure and Devices synchrotron facility. Previous scanning tunneling microscopy studies showed that a surface alloy phase seen at submonolayer coverages of Ag (<0.4 ML) evolves into well ordered Ag chains at higher coverages. These chains consist of Ag dimers and trimers directed on [001] of the substrate and located on monomer and dimer [001] directed vacancies.The ARUPS results for 1 ML coverage of Ag revealed that this unique chain geometry has near 1-dimensional electronic structure showing dispersion along the Ag-chains with no dispersion perpendicular to chains and no dispersion as a function of varying photon energy. The ARUPS were measured in two different geometries, specifically, the vector potential, A, was parallel and perpendicular to [001] plane of Cu(110) in which chain structure was directed. The energy distrubition curves (EDC) as a function of photon energy show the lack of dispersion which imply that Ag chains are not incorporated into Cu(110) substrate. Although no perpendicular dispersion is observed, ARUPS data confirms, by changing the emission angle in surface Brillouin zone along the two high symmetry lines, that the Ag bands in-plane (parallel to the surface) anisotropically disperse. In the experimental geometry probing electronic geometry parallel to the Ag structural chains, that is along the [001] direction of the substrate, the Ag bands disperse as a function of parallel momentum. In contrast, with the experimental geometry probing electronic structure perpendicular to the [001] direction, there is little to no dispersion of the Ag d-bands.These results signify reduced dimensional electronic structure of Ag chains. Research was supported by U.S. DOE contract No. DE-FG02-98ER45712.

9:00am **SS1-FrM3 Vacancies in Solids and the Stability of Surface Morphology***,* ***K.F. McCarty,*** *J.A. Nobel, N.C. Bartelt,* Sandia National Laboratories **INVITED**

We have examined the kinetics of island decay on the NiAl (110) surface using low-energy electron microscopy (LEEM). Remarkably, the decay rates are constant in time and totally independent of the local environment (e.g., the width of the immediately adja cent terraces and degree of island curvature). Given the lack of surface current between islands of different curvature, we conclude that surface diffusion is not important to the smoothing process. Instead, we find unambiguous evidence that bulk vacancie s are responsible -- we visibly observe exchange between bulk vacancies and the surface when the sample temperature is changed. For a temperature increase, the surface steps advance. For a temperature decrease, the surface steps recess. These changes result from the increase (decrease) in bulk vacancy concentration for a temperature increase (decrease). Remarkably, the size change accompanying a temperature change is strictly proportional to the perimeter (step length) of the island, and again is totally independent of the local environment. Thus, we conclude that the atoms at surface steps undergo direct exchange with bulk vacancies. We will present simple mathematical models showing how this mechanism quantitatively describes the constant-rate kinetics as well as the bulk-derived flux associated with a temperature change. The complete independence of the surface dynamics on the local environment results from the fact that the steps are interacting directly with the bulk, and thus, the local step density and curvature are largely irrelevant. We will also present results illustrating how the bulk/surface exchange affects NiAl oxidation. This work was performed under the U.S. Department of Energy contract DE-AC04-94AL85000 and supported by the Office of Basic Energy Sciences-Division of Materials Sciences.

9:40am **SS1-FrM5 Surface Freezing in Binary Metallic Melts***,* ***A. Turchanin,*** *W. Freyland, D. Nattland,* University of Karlsruhe, Germany

We report on a new phenomena of surface freezing, whereby an ordered solid film forms on top of the bulk liquid at temperatures above the bulk crystallisation. Recently this phenomenon has been observed in dilute Ga-Pb@footnote 1@ and Ga-Bi@footnote 2@ liquid alloys. Here we present new results on the investigation of surface freezing in the entire composition range of the Ga-Bi system. Second Harmonic Generation and Plasma Generation methods were applied to distinguish between the solid and liquid states of the alloy surfaces as a function of temperature and composition. The surface freezing was detected for all investigated alloys with composition between the eutectic (x(Bi)=0.0022, T(eut)=29.48°C) and monotectic point (x(Bi)=0.085, T(mono)=222 °C). On cooling of such alloys a Bi-rich solid-like film forms on top of the bulk liquid phase at temperatures well above the liquidus line. This film disappears on heating at higher temperatures, which characterizes this transition as a first-order phase transition. The maximum difference between the liquidus temperature and the temperature of the surface freezing transition was detected for the eutectic alloy (T(tr)-T(eut)=20 K). The lines of surface freezing and respective melting merge with the liquidus line approaching the monotectic point. The thickness of the forming Bi-rich solid-like films estimated from our measurements lies in the ranges from 0.5-1 nm to 100 nm. We have indications that it has a tendency to increase approaching the monotectic point. The relation of the surface freezing and wetting transitions occurring in Ga-Bi will be discussed. The surface freezing in Ga-Bi system will be compared with the two-dimensional freezing in dilute Ga-Pb alloy detected by x-ray reflectivity and grazing incidence diffraction methods.@footnote 1@ @FootnoteText@ @footnote 1@B. Yang, D. Gidalevitz, D. Li, Z. Huang, S.A. Rice, Proc. Nat. Acad. Svi USA, 96 (1999) 13009 @footnote 2@A. Turchanin, D. Nattland, W. Freyland, Chem. Phys. Lett. 337 (2001) 5.

10:00am **SS1-FrM6 Submonolayer Growth of Ag on Pt(100): Competition between Alloying and Surface Reconstruction***,* ***M. Batzill,*** *B.E. Koel,* University of Southern California

The growth of Ag on Pt(111) and the formation of a nanophasic alloy, has been thoroughly studied. On the Pt(100) surface, the presence of the energy-minimizing, hex-reconstruction gives rise to phenomena different to that on the (111) face. We present STM, AES, and TPD studies of the Ag/Pt(100) interface for submonolayer Ag coverages in a temperature regime between 300 and 900 K. We observe strongly anisotropic growth of Ag islands governed by the anisotropy of the reconstructed surface at 300 K. Adsorption of Ag lifts the reconstruction, resulting in a kinetically trapped Ag80Pt20 alloy formed by using the excess Pt from the reconstruction ejected into the growing Ag-islands. Annealing causes diffusion of Ag from the Ag80Pt20 adislands to the pure Pt(100) reconstructed regions, lifting its reconstruction and forming a nanophasic Ag-Pt alloy. For surfaces with less than 0.3 ML Ag, domains of Pt(100)-hex reconstruction and a Ag30Pt70 alloy coexist in thermodynamic equilibrium. This phase segregation is a result of energy minimization, and can be explained by the presence of two minima in the Ag-Pt surface phase diagram associated with the pure Pt reconstruction and a strain stabilized alloy phase. Deposition of more than 0.3 ML increases the Ag content in the alloyphase until no Pt remains in the monolayer and an abrupt Pt/Ag interface forms.

10:20am **SS1-FrM7 Direct Observation of Surface Alloying and Interface Roughening: Growth of Au on Fe(001)***, M.M.J. Bischoff, T. Yamada, A.J. Quinn, R.G.P. van der Kraan,* ***H. van Kempen,*** University of Nijmegen, The Netherlands

Iron and gold belong to the family of elements which do not form alloys because of the large size difference of the Fe and Au atoms. Nevertheless, it has been predicted by Tersoff@footnote 1@ that for those elements surface confined mixing may generally occur. In the low coverage limit, this might lead to surface alloying. Because of the immiscibility of these elements, an interesting question is what will happen when this surface alloy becomes saturated, i.e. more Au is deposited than allowed for a surface confined alloy. The Au/Fe combination is especially suitable for the detailed study of possible interface processes like segregation and interface diffusion. The reason is that, while the in-plane lattice match is nearly perfect, there is a large difference in the out-of plane distance between the bcc Fe and the fcc Au (0.14 nm compared to 0.20 nm). This allows to discriminate between interface and surface features. In this paper, we report a scanning tunneling microscopy study on the growth of Au on Fe(001) at 500K. Deposition of 0.5 monolayer (ML) leads to complete coverage by a homogeneous alloyed monolayer and simultaneous formation of islands covering 50% of the terraces. Consecutive deposition of more Au leads to demixing: in this process Au islands embedded in the original Fe(001) terrace are created while Fe islands stick out in the Au covering layers. By using suitable chosen growth and anneal temperatures, the processes at the interface can be followed even for thicker coverages of 5 ML. Scanning tunneling spectroscopy studies on this system will be presented: a new surface state around 0.6-0.7 eV is detected on the homogeneous alloyed surface layer. @FootnoteText@ @footnote 1@J. Tersoff, Phys. Rev. Lett. 74, 434 (1995).

10:40am **SS1-FrM8 Surface Reconstruction STM Studies of Clean and Oxidized Low Index FeAl Surfaces***,* ***O. Kizilkaya****, D.A. Hite,* Louisiana State University*; D.M. Zehner,* Oak Ridge National Laboratory*; P.T. Sprunger,* Louisiana State University

Details of the atomic reconstruction behavior of clean and oxidized (110), (210) and (310) surfaces of the ordered bimetallic alloy FeAl has been studied with STM. Prefentially sputtering impedes the aluminum concentration on the surfaces. Aluminum preferentially segregates to the surface layer upon sequential annealing of these low index surfaces. Depending on the annealing temperature, there are a sequence of differing surface reconstructions on FeAl(110). At 400 C, a bulk terminated surface is observed. Between the temperatures range of 400-600 C and 800-1000 C an incommensurate FeAl2 overlayer is obtained. At annealing temperatures of 600-800 C, STM images reveal a long-range missing row reconstruction parallel to the [001] direction. For a wide range of annealing temperatures, FeAl(210) reconstructs to a (1x3) structure. The surface has alternating (100) and (110) facets. A similar type of reconstruction is observed for FeAl(310); however, the surface is not stable but facets. The crystal miscuts and kinetic effects are the main reason for instability. In the case of oxidized FeAl(110), STM reveals the formation of a thin-film gamma-alumina at low coverages. This structure is characterized as a hexagonal moir@aa e@ pattern with a spot-spot distance of 1.8 nm. Research conducted at Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy, under contract DE-AC05-00OR22725. Research was supported by U.S. DOE contract No. DE-FG02-98ER45712.

11:00am **SS1-FrM9 Self-Assembly of Nanoscale Hexagons in S/Cu/Ru(0001)@footnote 1@***,* ***A.P. Baddorf,*** Oak Ridge National Laboratory*; H. Zajonz, D. Gibbs,* Brookhaven National Laboratory

Periodic structures on a nanometer length scale exhibit unique dynamics and forces, and offer a template for ordering of quantum dots. Recently, Hrbek, et al.,@footnote 2@ have shown that small quantities of S adsorbed on the two layer Cu/Ru stripe phase react at dislocations, shorten stripes, and produce a quasi-hexagonal structure. We have examined the growth of this structure and its dependence on temperature with synchrotron x-ray diffraction. Deposition rates were determined by monitoring the intensity at the specular anti-Bragg position (similar to RHEED oscillations). After S deposition of up to 0.2 ML at room temperature, no new diffraction was observed, even after annealing. This is consistent with the results of Hrbek, et al., who found poor order in STM images. For deposition between 100 and 200°C, additional reflections were observed corresponding to a quasi-hexagonal lattice with a periodicity of approximately 44 Å. This structure persisted when the sample was cooled to room temperature. Long range order was indicated by narrow peak widths, 0.009 Å@super -1@ FWHM, corresponding to a correlation length of over 700 Å. Heating above 200°C reduced and broadened the diffraction wavevector, indicating a larger, less ordered lattice. Above 300°C, the quasi-hexagonal diffraction pattern disappeared leaving only diffraction from the linear Cu/Ru stripe phase. This process was reversible, so that cooling below 300°C returned the hexagonal pattern. We interpret this as a melting of the S induced structure. @FootnoteText@ @footnote 1@ORNL is managed by UT-Battelle, LLC under US DOE contract DE-AC05-00OR22725. BNL is supported by US DOE DE-AC02-98CH10886. @footnote 2@J. Hrbek, J. de la Figuera, K. Pohl, T. Jirsak, J. A. Rodriguez, A. K. Schmid, N. C. Bartelt, and R. Q. Hwang, J. Phys. Chem. B 103, 10557 (1999).

11:20am **SS1-FrM10 Application of EELFS Spectroscopy to Local Atomic Structure Study***,* ***Yu.V. Ruts****, A.N. Maratkanova, D.V. Surnin, D.E. Guy,* Physical-Technical Institute of Ural Branch of RAS, Russia

Fine structures above ionisation edges studied in the EELFS (Extended Energy Loss Fine Structure) technique are similar to those measured in X-ray absorption spectra (EXAFS). A possibility to measure extended structures using both transmission and reflection modes allows to obtain not only bulk parameters of the local atomic structure (partial interatomic distances, coordination numbers, backscattering amplitudes, phase shifts, etc.) but also the surface ones. Surface sensitivity makes the EELFS technique competitive with diffraction techniques especially for studying systems without long-range order. Moreover the EELFS spectroscopy is available in most surface and material physics laboratories having standard equipment with the electron exitation. In contrast to EXAFS the EELFS technique makes possible to study local domains, for example individual blocks or grains, owing to using an electron beam as an exciting source. The essential peculiarity of this method is its high sensitivity to light elements. This is very important for studying surface and bulk oxides, carbides and so on as well as the processes of their formation including gas adsorption. EELFS technique has been proved to be a powerful tool for local structural investigations of clean surfaces and chemisorbed species. Numerous papers have been published to demonstrate the applicability of the EELFS technique in the determination of the structure of different compounds and different metals deposited on clean surfaces. Application of the EELFS technique provides great progress to materials science in regards to atomic structure study. In this paper we give some examples of studying different materials by the EELFS both in transmission and reflection mode using the results obtained by different authors including our own ones. This work was sponsored in part by the Russian Foundation for Basic Research (grants 00-03-33049a and 00-15-97419).

Surface Science
Room 121 - Session SS2-FrM

Gas-Solid Dynamics: Theory and Experiment

Moderator: A.W. Kleyn, Leiden University

8:40am **SS2-FrM2 Chemisorption of O@sub2@ on Al(111): Non-Adiabatic Pathway to Abstraction, and Simulation of STM Data***,* ***J.Z. Sexton****, A.J. Komrowski, A.C. Kummel,* University of California, San Diego*; M. Binetti, O. Weisse, E. Hasselbrink,* Universitat Essen, Germany

There exists controversy in the literature surrounding the initial oxidation of the Al(111) surface. (1) DFT calculations show the activated reaction of O@sub2@ with Al(111) cannot be modeled using a single potential energy surface and consistency with the observed reaction barrier requires a non-adiabatic charge transfer process.@footnote 1@ The calculations show that the initial charge transfer is most favorable for end-on collisions with Al(111) which is consistent with an abstraction mechanism.@footnote 1@ (2) Abstractive chemisorption in the oxidation of aluminum is a process in which an oxygen molecule reacts with the surface producing one atom bound to the surface and one atom ejected into the gas phase. We have experimentally verified this mechanism using supersonic molecular beams to dose the clean Al(111) surface with variable incident energy O@sub2@. The evidence is as follows: (a) STM images show a transition between exclusively single O-adatom reaction products to more pairs of O-adatom reaction products as the O@sub2@ translational energy is raised from 0.025 eV (thermal) to 0.8 eV. (b) The ejected O-atoms have been detected in the gas phase with REMPI laser spectroscopy. This is consistent with an end-on, non-adiabatic reaction. (3) Interpretation of O-Al(111) reacted sites in STM images can be interpreted in terms of long range dissociation, abstraction, or diffusion.@footnote 2@ The main issue of the controversy is the assignment of single O-Al(111) reacted sites on the room temperature surface. We are performing cluster and slab calculations to simulate the appearance of O - Al(111) features in STM images. The existence of nearly degenerate adsorption sites for oxygen adatoms and local relaxation of the Al surface complicates the interpretation of the STM images. @FootnoteText@ @footnote 1@Y. Yourdshahyan, et al, Sol. St. Comm. 117, 531 (2001). @footnote 2@M. Schmid and P. Varga, in AVS Symposium Abstracts, SS-TuP4, Seattle, WA, (1999) p. 109.

9:00am **SS2-FrM3 Surface Temperature Effects in Molecular Beam Scattering: Inelastic State-to-state Scattering and the Dissociation of Hydrogen and Deuterium***, Z. Wang,* University of Texax, Austin*; G.R. Darling,* ***S. Holloway,*** University of Liverpool, UK

We have carried out quantum mechanical wavepacket calculations on a parameterized LDA potential energy surface for the surface temperature dependence of the inelastic scattering of hydrogen and deuterium molecules from Cu(111). We find, in agreement with experimental data, that the surface temperature dependence of each cross-section invariably has an Arrhenius form with an 'activation energy' that depends upon the translational energy of the molecules. Additional calculations for the dissociation probability reveal very similar results. On the basis of the wavepacket calculations, it has been possible to develop a simple model to explain the results. The model is quite general, robust and results will be presented for vibrationally inelastic scattering and dissociative adsorption. We shall discuss exactly the origins of the Arrhenius form for a system where thermal equilibrium is never established, and the meaning of the derived "activation energy" in terms of the parameters entering into the dynamical model.

9:20am **SS2-FrM4 Monte Carlo Simulation of the Adsorbate Assisted Adsorption in the Case of CO/ZnO***,* ***U. Burghaus,*** Ruhr-Universitaet Bochum, Germany

Very recently and for the first time the adsorption dynamics of a prototype molecule has been studied in detail on a metal oxide surface [Becker, Kunat, Boas, Burghaus, Woell, JCP 113 (2000) 6334], namely for the systems CO/O-ZnO and CO/Zn-ZnO, which both show a distinct increase in the adsorption probability with increasing CO coverage. This phenomenon (referred as adsorbate assisted adsorption) is in contrast to traditional precursor models. The presented Monte Carlo algorithm [submitted to Surf. Rev. and Lett.], which predicts the enhancement of adsorption by pre-adsorbates, assumes different adsorption probabilities for molecules scattered on bare and already occupied sites. Additionally, the effect of the mass-mismatch of the adsorbate and the surface atoms is considered. Thus, presented is an MC version of the analytical so-called modified Kisliuk model [e.g., R.J. Madix, et al., Surf. Sci. 470 (2001) 226]. In contrast to most of the analytic models, the MCS scheme includes lateral interaction energies, the influence of defects, and the effect of cooperative precursor dynamics. Although adsorbate assisted adsorption has also been observed on metal surfaces, the polar surfaces of ZnO are especially well suited to test the algorithm and the influence of the mass-mismatch on the energy transfer processes involved, since O-ZnO and Zn-ZnO differ solely by the mass of the atoms in the first surface layer. MC simulations will be presented which explain the main effects observed experimentally for both polar surfaces of ZnO.

9:40am **SS2-FrM5 Ultrafast Energy Flow Studied by Femtosecond Vibrational Spectroscopy***, S. Roke, A.W. Kleyn,* Leiden University, The Netherlands*;* ***M. Bonn,*** Leiden University, The Netherlands, Netherlands

We present a simple model describing femtosecond surface vibrational spectroscopy as a tool to study ultrafast surface chemical dynamics. We compare our calculations to recent experiments in which the interaction between CO and the Ru(0001) surface is studied using the femtosecond surface vibrational spectroscopy: sum frequency generation (fs-SFG). After short-pulsed excitation of the metal leading to desorption of CO, a transient red-shift and broadening in the infrared spectrum of the C-O stretch vibration on a picosecond time-scale are observed. The data are successfully modeled by considering the response of adsorbed CO to heating of the system by a femtosecond laser pulse. The calculations match the experimental data very well and demonstrate that fs-SFG is a very powerful tool to study the dynamics of molecules at surfaces. Detailed analysis shows that this method will enable us to detect transition states and reaction intermediates in chemical reactions at surfaces and determine the transition state lifetime. Results of first experiments on energy flow in a reacting system will be shown at the meeting.

10:20am **SS2-FrM7 Vibrational Energy Transfer and Energy "Pooling" in Adsorbate Layers: CO on NaCl***, S.A. Corcelli,* ***J.C. Tully,*** Yale University **INVITED**

Adsorbate vibrational excitations on insulator surfaces can be very long-lived if the adsorbate frequency is much greater than the Debye frequency of the solid. This allows time for vibrational excitations to resonantly hop among neighbors a great many times before de-excitation. Sometimes this will result in two adjacent adsorbate molecules both excited to v=1. As a result of anharmonicity, the state with one molecule in v=2 and one in v=0 has a slightly lower energy than both molecules in v=1. Similarly, 3 quanta of vibration shared by two neighboring adsorbate molecules produce a lower total energy if all 3 quanta reside on one of the neighbors. This produces a driving force for "pooling" of energy into highly excited molecules. This effect has been demonstrated dramatically by George Ewing and coworkers@footnote 1@ who observed population of vibrational levels as high as v=15 for CO on NaCl. We have developed a perturbation theory approach to calculate all of the operative rate processes; vibrational relaxation, resonant hopping, pooling, and radiation. We have used these rates in a kinetic Monte Carlo simulation of the energy pooling process. Our results are in qualitative agreement with experiment, and reveal interesting phenomena such as self-trapping and Ostwald ripening. In addition, we predict an enormous C-12/C-13 isotope effect. @FootnoteText@ @footnote 1@ H.-C. Chang and G. E. Ewing, Phys. Rev. Lett. 65, 2125 (1990).

11:00am **SS2-FrM9 HD Scattering on Cu (001): Rotationally Mediated Bound State Resonances and Evidence for Interaction of the Bound States with the Surface Phonons***,* ***L.V. Goncharova,*** *A.V. Ermakov, B.J. Hinch,* Rutgers University

Seeded HD molecular beams have been used to study the laterally averaged HD - Cu (001) physisorption potential by measurements of rotationally mediated bound state resonances (BSR). The physisorption well depth of 30.5 meV was confirmed using a Le Roy plot by combining our HD data with existing H@sub 2@ and D@sub 2@ data. The positions of all rotationally mediated bound state resonance energies are determined well by the results of calculations using different potentials. BSR energies from isotropic potential calculations are considerably higher than the experimentally determined energies, as well as those of the values calculated with an anisotropic potential. So the anisotropic part of the potential cannot be neglected. Calculations predict lower energy for m@sub J@ = 0, indicating that the molecule prefers to have its molecular axis perpendicular to the surface (cartwheel rotation). A considerable shift of the bound state levels in the presence of an adsorbate (chemisorbed hydrogen) is also observed. Resonance energies do not change with the surface temperature. The Debye-Waller analysis of the intensities and the widths of the resonance features show a coupling between the resonant states and surface phonons. The strongest coupling is for the states lower in the potential well.

Surface Science

Room 122 - Session SS3-FrM

Clean and Adsorbed Surfaces

Moderator: J.A. Yarmoff, University of California, Riverside

8:20am **SS3-FrM1 Structure and Electronic Properties of Planar and Faceted Ir(210)***,* ***I. Ermanoski,*** *M. Gladys, G.J. Jackson, T.E. Madey,* Rutgers, The State University of New Jersey*; J.E. Rowe,* U.S. Army Research Office

The atomically rough Ir(210) surface is morphologically unstable: When Ir(210) is covered with more than 0.6 ML of oxygen and annealed, pyramidal facets develop on the initially planar surface. We have used a variety of methods to investigate the structure and electronic properties of planar and faceted Ir(210), including LEED, STM and high resolution soft X-ray photoelectron spectroscopy (SXPS) using synchrotron radiation. To prepare an oxygen-free faceted surface, we use catalytic CO oxidation at ~500 K to react the oxygen off the pre-prepared faceted surface. Cleanliness is verified both by AES and TPD. LEED and STM experiments show that the faceted surface is entirely covered with 3-sided pyramidal facets with dimensions of several nanometers. HRSXPS has been employed to investigate core-level features of all the surfaces mentioned. The Ir 4f7/2 core levels are fitted with Doniach-Sunjic lineshapes. Surface and bulk peak identifications are supported by measurements at different photon energies (different electron escape depths) and variable photoemission angles. All of the surface components (first, second and third layer peaks) are identified with core-level shifts positioned at higher binding energies with respect to the bulk. This result is in contrast to previous reports of binding energy inversion on Ir(100) and Ir(111) surfaces. The adsorption of oxygen onto the planar Ir(210) surface causes a suppression and shifting of the surface features. A comparison of planar and faceted surfaces reveals only minor differences in the SXPS core-level spectra. The effect of metallic overlayers on the morphological stability of Ir(210) will also be discussed. Supported by US DOE and ARO.

8:40am **SS3-FrM2 Linking Stress to Surface Structure Using STM***, **G.E. Thayer**[1], *UC Davis and Sandia National Labs*; N.C. Bartelt, V. Ozolins,* Sandia National Laboratories*; A.K. Schmid,* Lawrence Berkeley National Lab*; S. Chiang,* University of California, Davis*; R.Q. Hwang,* Sandia National Laboratories

Understanding the role of stress at solid surfaces is necessary to determine why surfaces have particular structures. While significant progress has been achieved in considering how local elastic interactions might contribute to the total surface energy and structure, it had not been possible to explicitly confirm this experimentally. The main reason for this is the difficulty in measuring stress fields on surfaces. Here, our approach has been to directly measure strain fields on a surface arising from lattice mismatch. Studying the phase diagram of CoAg/Ru(0001) single-monolayer films using STM, we found that annealed Co-rich films form an alloy with a structure that is not atomically mixed but instead consists of Ag droplets (15-30 atoms in size) with in a Co matrix. To quantitatively answer the question of how surface stress contributes to the formation of this structure, we have directly probed the stress fields on the surface. Analysis of atomically resolved images of the CoAg alloy has allowed us to perform strain measurements over the surface. In our analysis we have compared strain measurements of about 800 Co atoms in a wide variety of Co-Ag neighborhoods with calculations of strain resulting from the Frenkel-Kontorova (FK) model and first-principles local spin density approximation (LSDA) calculations. The close agreement between the measurements and the calculations explicitly shows how stress due to lattice mismatch contributes to the formation of the droplet structure of the alloy. Within the framework of the FK model we determine the relative forces acting on the surface by the measurement of strain fields and we are able to provide a direct link between surface stress and surface structure. We find the agreement even allows for the determination of details such as elastic spring constants from experimental measurements. Our success firmly demonstrates the possibility of using atomically resolved STM data to investigate surface stress.

9:00am **SS3-FrM3 In-Situ STM Study of the Au(111) Herringbone Reconstruction Under Applied Stress***, O. Schaff,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany*; **A.K. Schmid,*** Lawrence Berkeley National Laboratory*; N.C. Bartelt, J. de la Figuera, R.Q. Hwang,* Sandia National Laboratories

Surface stress is generally invoked as the driving force for the remarkably well-ordered and stable dislocation networks or reconstructions found in the surface layers of many epitaxial thin films, as well as in many metal single-crystal surfaces. To test this conjecture, the effect of uniaxial applied stress on dislocation networks present in the atomic surface layer of Au(111) was studied. The measurements were made using a novel instrument combining ultrahigh vacuum scanned-probe microscopy with an in-situ stress-strain testing machine. The technique provides microscopic information, up to atomic resolution, about the large-scale plasticity of surface layers under applied loads. The herringbone reconstruction of the Au(111) surface is a classic example of a strain stabilized dislocation network. We find that under 0.5% uniaxially applied compressive strain a dramatic restructuring of the network takes place. The three-fold orientational degeneracy of the system is removed and threading edge dislocations are annihilated. By considering the energetics of the herringbone reconstruction in the context of the Frenkel-Kontorova model, we are able to explain why these changes take place at this value of the applied strain.

9:20am **SS3-FrM4 Core Level Shifts and Stress at the Ni/W(110) Interface@footnote *@***, **R.T. Franckowiak,*** Utah State University*; N.D. Shinn,* Sandia National Laboratories*; B. Kim, K.J. Kim, T.-H. Kang,* Pohang Light Source, South Korea*; D.M. Riffe,* Utah State University

Stress can play an important role in determining the structure and stability of heterogeneous interfaces. A recent STM and strain study@footnote 1@ of Ni overlayers on W(110) identified a pseudomorphic (1x1), and incommensurate (8x1) and (7x1) phases that exhibit compressive, tensile, and compressive stress, respectively. Interfacial electronic structure was suggested as the origin of the unexpected compressive stress in the (1x1) phase, rather than simple lattice mismatch in the adsorbed Ni film. This hypothesis was tested by measuring the W(4f) core-level binding energy shifts of interfacial W atoms during Ni overlayer growth. Photoemission spectra were obtained at the National Synchrotron Light Source, Brookhaven National Laboratory, using photon energies between 60 at 110 eV at a resolution of 150 meV. For the compressive pseudomorphic phase, interface W atoms exhibit a shift (compared to the bulk W) of -210 meV, whereas the 8x1 and 7x1 phases induce much smaller shifts of -90 and -120 meV, respectively. These shifts, which cannot be interpreted in terms of simple W-Ni coordination arguments, suggest that the interface tungsten electronic structure is very different in the pseudomorphic phase compared to the denser phases, and thus may be the source of the stress observed in the pseudomorphic phase. The similar W(4f) shifts in the 8x1 and 7x1 phases, which exhibit tensile and compressive stress, indicate that these stresses result from the Ni adlayer, as is expected from simple strain arguments based on the bulk Ni lattice constant. @FootnoteText@ @footnote 1@D. Sander, C. Schmidthals, A. Enders, and J. Kirschner, Phys. Rev. B 57, 1406 (1998). @footnote *@Supported by the DOE-BES Division of Materials Sciences. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

9:40am **SS3-FrM5 Metal Nucleation and Adhesion on Ionic-Oxide Terraces****, **D.R. Jennison,*** Sandia National Laboratories*; A. Bogicevic,* Ford Research Laboratory*; A.E. Mattsson,* Sandia National Laboratories

We present two topics: First, it has recently been proposed@footnote 1@ that oxide surfaces with a substantial number of oxygen vacancies may show greatly increased adhesion. It has also been observed that metal islands nucleate not only at line defects, but also on oxide terraces. Using first-principles DFT, we previously@footnote 2@ studied the Pt dimer on MgO(100), and found that neither the O nor the Mg vacancy increased its stability, and in fact the dimers were only marginally stable at room temperature. We have now extended this study to include the dimers of eight different metals, both on the clean surface and at the O vacancy. We find that not all metals behave similarly! In fact, the dimers of Ag and Au are much more tightly bound on the clean surface than are those of Pd or Pt, and actually increase their stability at the defect. We understand these results based on dimer electronic structure. The second topic concerns the accuracy of DFT for studies of metal/oxide interfaces where the metal binds mostly by polarization, i.e. where there are no significant chemical bonds. This bonding is much stronger than van der Waals and it is measurable by analysis of the Wulff shapes of metal nanoparticles.@footnote 3@ In the cases of Pd and Cu on alumina films, DFT in the LDA predicts a work of adhesion close to experiment,@footnote 3@ while the GGA fails badly (and differs by about 50%). We have now understood this unusual failure of GGA in terms of the surface self-exchange error in DFT, as evidenced recently for another metal.@footnote 4@ In fact, the experimental result, vs. the computational numbers, supports our previous assertion@footnote 5@ that the interfacial binding of most metals on ionic oxides is mainly due to polarization. @FootnoteText@@footnote 1@Y. F. Zhukovskii, et al., PRL 84 (2000) 1256. @footnote 2@A. Bogicevic and D. R. Jennison, Surf. Sci. 437 (1999) L741. @footnote 3@K. H. Hansen, et al., PRL 83 (1999) 4120; T. Worren et al., Surf. Sci. 477 (2001) 8. @footnote 4@K. Carling, et al., PRL 85 (2000) 3862. @Footnote 5@C. Verdozzi, et al., PRL 82 (1999) 4050; A. Bogicevic and D. R. Jennison, PRL 82 (1999) 799. *Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000; www.sandia.gov/surface_science/drj/.Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000; www.sandia.gov/surface_science/drj/.

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[1] **Morton S. Traum Award Finalist**

10:00am **SS3-FrM6 Structure Analysis of Oxygen-adsorbed and Annealed W(001) Surface at Liquid Nitrogen Temperature***, S. Kamimizu, K. Hara, T. Kokubun, T. Haga, K. Sakamoto,* ***H. Yamazaki,*** The University of Electro-Communications, Japan

The structure of oxygen-adsorbed and annealed W (001) surface was investigated at the liquid nitrogen temperature. We have already reported the structure of this system at the room temperature (H. Yamazaki, et al., Surf. Sci. 447 (2001) 174). The result obtained previously is that the 2x1 LEED pattern was observed, and the most probable calculated structure consists of missing rows of W and double rows of oxygen atoms adsorbed on one of two three-hold hollow sites of W (011) facet which was appeared by losing the W-atoms. The Pendry R-factor for this structure is 0.25. As the energy difference between those two three-hold hollow sites is so small as 12 meV by a rough calculation, the adsorbed oxygen atoms should occupy those two sites by a certain ratio. It is considered that the oxygen atoms fall into the more stabilized adsorption site when the sample is cooled down to the liquid nitrogen temperature. Then the experiment was performed on the same sample at the liquid nitrogen temperature, and the most probable structure was determined with the Pendry R-factor of 0.20. The structure agrees well with that at the room temperature within an error. We will present the experimental and calculating procedure, and the most probable structure compared with that at the room temperature.

10:20am **SS3-FrM7 The Local Adsorption Structure of CH@sub 3@- on Cu(111)***, M. Pascal, C.L.A. Lamont,* University of Huddersfield, UK*;* ***J. Robinson****, R.L. Toomes, J.-H. Kang, D.P. Woodruff,* University of Warwick, UK*; L. Constant, S. Bao, M. Kittel, J.-T. Hoeft, M. Polcik,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

Methyl is an important intermediate in many surface reactions, but there is a dearth of information on its local adsorption geometry. We present the results of both experimental and theoretical studies of the structure of CH@sub 3@- on Cu(111). The experiments were based on C 1s scanned-energy mode photoelectron diffraction (PhD) from a surface formed either by exposure to CH@sub 3@- ions from a Bent-type azomethane (CH@sub 3@-N-N-CH@sub 3@) cracking source, or from surface dissociation of methyl iodide (CH@sub 3@I) on the surface. The coadsorbed I , which occupies the fcc hollow sites (directly above a third layer Cu atom) appears to have little effect on the geometry of the methyl which also occupies an fcc hollow site but shows a marginally (0.04±0.03 Å) smaller layer spacing relative to the substrate in the presence of the coadsorbate. In the pure methyl layer the C-Cu outermost layer spacing is 1.66±0.02Å. Density-functional theory results (using the CASTEP code in GGA with ultrasoft pseudopotentials) reproduce the preference for hollow site adsorption (albeit with a very small preference for the hcp hollow) but also reveal a strong preference for an azimuthal orientation in which the C-H bonds are oriented along the Cu-Cu close packed directions, placing the H atoms closer to near-neighbour Cu atoms.

10:40am **SS3-FrM8 Cu(100)c(2x2)-N: a New Type of Adsorbate-Induced Surface Reconstruction***, S.M. Driver,* University of Warwick, UK*; J.-T. Hoeft, M. Polcik, M. Kittel, R. Terborg,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany*; R.L. Toomes, J.-H. Kang,* ***D.P. Woodruff,*** University of Warwick, UK

Using a combination of N 1s scanned-energy mode photoelectron diffraction and scanning tunnelling microscopy the Cu(100)c(2x2)-N surface is shown to undergo a symmetry-lowering reconstruction with a large amplitude (0.34 Å) periodic distortion of the outermost Cu layer perpendicular to the surface. This contrasts with the more usual surface layer density changes or parallel distortions which are the primary characteristic of other metal surface reconstructions. Atomic resolution imaging under varying tip conditions shows that in the c(2x2) phase STM appears to always image as asperities the Cu atoms, and not the N atoms, and that the N induces the unusual rumpling of the outermost Cu layer. This structural modification is quantified by the PhD data. Our STM images also provide a clear demonstration of the dangers of an over-simplistic interpretation of such data in terms of adsorbate atomic coordinates. The presence of the rumpling reconstruction, which we attribute to N-induced compressive surface stress, allows one to understand many detailed aspects of the mesoscopic c(2x2) island structures observed in this system (and reported in earlier STM investigations). Not only can the general self-organisation be attributed to the minimisation of the long-range elastic strain field energy, but similar elastic strain arguments arising from local rumpling can account for the N-N attraction needed for the island formation. In addition, the symmetry-lowering nature of the reconstruction provides a simple explanation for the systematic width variations of the inter-island boundaries.

11:00am **SS3-FrM9 Phases of Oxygen on Cu(100) Imaged by Low Energy Electron Microscopy***,* ***C.L.H. Devlin,*** Air Force Research Laboratory, U.S.*; Y. Sato, S. Chiang,* University of California, Davis

Low energy electron microscopy (LEEM) was used to perform a detailed study of three phases of oxygen on the Cu(100) surface, including two new phases. These phases occurred when the sample was heated above 600°C. Dark field imaging was used to identify regions corresponding to particular low energy electron diffraction (LEED) patterns. The structure of the steps was also examined in the LEEM images of the different phases. At low coverage, the familiar (@sr@2x2@sr@2)R45° structure was observed. When annealed to 600°C, the steps changed from being gently curving to being highly bunched and completely straight with 90° kinks, resulting from a disorder-order transition. At higher oxygen coverage, <1.8ML, a new, complicated LEED pattern emerged, consisting of the (@sr@2x2@sr@2)R45° pattern plus a centered rectangular structure. Images of this surface included decoration of step edges and bright, sometimes hatched, areas on the terraces. Distinct bunching of steps, which curved gently over many microns, occurred. At higher coverage, <3.2ML, another new LEED pattern occurred. The "12-spot" hexagonal pattern corresponds to a hexagonal phase with two domains. The lattice constant of this structure agrees well with that for Cu@sub 2@O, suggesting that this phase corresponds to multilayers of cuprous oxide. LEEM imaging was used to follow structural transitions among the three phases.

11:20am **SS3-FrM10 Temperature Dependence of Oxides on Titanium Surface in UHV***,* ***Y. Mizuno,*** Chiba Institute of Technology, Japan*; A. Tanaka,* ULVAC-PHI, Inc.*; Y. Takakuwa,* Tohoku University, Japan*; T. Momose,* Miyagi National College of Technology, Japan*; Y. Yamauchi,* Chiba Institute of Technology, Japan*; T. Homma,* Chiba Institute of Technology

It is well known that titanium has a good ability to passivate a surface, and as a result to exhibit a high degree of immunity against attack by acids and chlorides, although the titanium surface is very active such as a gettering property. Titanium has stable oxides which are Ti@sub 2@O, TiO, Ti@sub 2@O@sub 3@, Ti@sub 2@O@sub 5@, Ti@sub n@O@sub 2n-1@(4<n<38) and TiO@sub 2@. The temperature dependence of titanium oxides was investigated in-situ with using Auger electron spectroscopy (AES) with quadrupole mass spectrometer (QMS) and X-ray photoelectron spectroscopy (XPS) at a temperature range RT-500 °C. The surface of specimen was prepared by electro-polishing, and on the surface thin titanium oxide layer was formed, although the oxide was mainly TiO@sub 2@. As the temperature of titanium surface increases, over 300 °C, O@sub KLL@ Auger intensity decreases in a drastic way, and in contrast Ti@sub LMM@ Auger intensity increases. Over 450 °C, no oxygen was detected on titanium surface in UHV. However, outgassing rates of O@sub 2@, CO, and CO@sub 2@ from the titanium surface did not show large changes in QMS measurements below 450 °C. This behavior is explained such as a gettering property, which is an enhancement diffusion of oxygen from a surface to bulk. In order to investigate temperature dependence on the chemical states of titanium, XPS analysis was performed in-situ at a temperature range between RT - 500 °C. The results showed drastic changes of titanium oxides which the suboxides began to decrease at 150 °C, even the amount of TiO@sub 2@ decreasing over 200 °C. Titanium has a very sensitive oxide surface depending on temperature in UHV.

Thin Films

Room 123 - Session TF-FrM

Diamond and Related Materials

Moderator: B.C. Holloway, College of William & Mary

8:20am **TF-FrM1 Synthesis and Characterization of Highly Conducting Nitrogen Doped Ultrananocrystalline Diamond Films***,* ***J. Birrell,*** *O. Auciello, S. Bhattacharyya, J.A. Carlisle, L.A. Curtiss, A.N. Goyette, D.M. Gruen, J. Schlueter, A.V. Sumant, P. Zapol,* Argonne National Laboratory

Diamond has many superior materials properties, yet its application in electronic devices is severely limited due to the difficulty of producing n-type thin films of sufficiently high conductivity. In this work ultrananocrystalline diamond (UNCD) films with up to 0.2% total nitrogen content were synthesized by a microwave plasma enhanced chemical vapor deposition (MPCVD) method using a CH@sub 4@ (1%)/Ar gas mixture with 1-20% nitrogen gas added. CN and C@sub 2@ radicals are identified in the plasma and both their relative and absolute concentrations change as N@sub 2@ gas is added. The morphology and transport properties of the films are both greatly affected by the presence of CN. High-resolution TEM data indicated that the grain size and GB width increase with the addition of more than 5% N@sub 2@ in the plasma. The electrical conductivity of the nitrogen-doped UNCD films increases by five orders of magnitude (up to 143 @ohm@@super -1@ cm@super -1@) with increasing nitrogen content. Conductivity and Hall measurements made as a function of film temperature down to 4.2 K indicate that these films have the highest n-type conductivity and carrier concentration demonstrated for phase-pure diamond thin films. Grain-boundary conduction is proposed to explain the remarkable transport properties of these films, in which nitrogen segregates to the grain-boundaries and promotes sp@super 2@ bonding and the introduction of more states into the fundamental gap, leading to enhanced electron transport. Work supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38.

8:40am **TF-FrM2 Probing Surface Species on a Diamond C(111) Surface During the Chemical Vapour Deposition of Diamond***, A. Heerwagen, M.T. Strobel, M. Himmelhaus,* University of Heidelberg, Germany*; **M. Buck,*** University of St Andrews, Scotland

The bottleneck in the accurate modeling of the diamond growth by chemical vapour deposition (CVD) is the lack of knowledge of the surface species and chemistry. In contrast to the gas phase, there is a deficit in experiment data for chemical species and reactions associated with the surface of a growing diamond film. The reason for this striking imbalance between experimental data on the gas phase and the surface lies in the diffculty to probe surface species in situ under the conditions of diamond CVD. Under these conditions, which are prohibitive for other surface science techniques we have applied IR-visible sum frequency generation (SFG) to probe the surface of a natural diamond during the CVD process, using a hot filament (HF) reactor and a gas mixture of hydrogen and methane. Monitoring the range of the C-H stretching vibrations, a single band reflecting a monohydrogen termination of the diamond substrate surface is observed under conditions which yield high quality diamond films. A decrease of the filament temperature from 2000Â°C to 1850Â°C leads to a decrease in intensity of this peak appearing around 2820 cm-1. At filament temperatures below 1800Â°C a new band at 2809 cm-1 emerges while the peak at 2820 cm-1 vanishes. Lowering the substrate temperature has a minor influence on this spectral feature but, instead, a new band at 2855 cm-1 appears. Changing the composition of the gas phase causes the intensity and frequency of the monohydrogen band to vary significantly. In particular, in a pure hydrogen atmosphere it blue-shifts to 2830 cm-1 while a pronounced increase in intensity is detected. Comparison of these results with previous SFG data obtained under ultra high vacuum reveals pronounced similarities. Furthermore, the identification of the species and surface structure associated with the peak at 2855 cm-1 seems to be vital for improving the quality of CVD diamond films grown at lower temperatures.

9:00am **TF-FrM3 Structural, Mechanical and Electrical Properties of DLC Films Deposited by DC Magnetron Sputtering***, **E. Broitman,*** College of William and Mary*; Zs. Czigány, L. Hultman,* Linköping University, Sweden*; B.C. Holloway,* College of William and Mary

The microstructure, morphology, growth rate, surface roughness, surface energy, electrical and mechanical properties of diamond-like carbon (DLC) films deposited by direct current (d.c.) magnetron sputtering on Si substrates at room temperature were investigated. Film properties were found to vary markedly with the pressure (P@sub Ar@), bias voltage (V@sub B@), and discharge current (I@sub T@). Plan-views HRTEM revealed an amorphous microstructure, however cross-sectional SEM shows a columnar structure at the higher V@sub B@. Film stresses were found to be compressive in all cases, increasing from 0.5 GPa for grounded substrates to 3.5 GPa for films deposited at V@sub B@ = - 90 V and I@sub T@ = 0.3 A. Film stress was not affected by V@sub B@ at I@sub T@ = 0.9 A. The hardness (H), Young's moduli (E) and elastic recovery (R) increased with V@sub B@ to maximum values of H = 27 GPa, E = 250 GPa, and R = 68 %. With an increase in the negative bias, the resistivity @rho@ went through a maximum of 2.2 @ohm@cm at potentials around the floating potential U, while @rho@ decreased with the increase of pressure or discharge current. Langmuir probe measurements of the local electron temperature, density, and plasma potential as a function of Ar pressure and target current were also made at the substrate location. The properties of the films have been correlated in terms of differences in the deposition and plasma parameters.

9:20am **TF-FrM4 Electron Transmission in Thin B-doped CVD Diamond Films***, **J.E. Yater**, A. Shih, J.E. Butler, P.E. Pehrsson,* Naval Research Laboratory

Diamond is a promising cold emitter material for vacuum electron devices because of the negative electron affinity (NEA) observed at specific surfaces. While the NEA properties have been studied extensively, the cold emission process in diamond has not been well characterized. In this study, we inject electrons into thin CVD diamond films using a 0-20 keV electron gun, and we examine the transport and emission of low-energy secondary electrons in transmission measurements. In particular, we measure the intensity and energy distribution of transmitted electrons as a function of incident beam parameters (energy, current) and material properties (film thickness, doping concentration). A series of B-doped CVD diamond films has been grown with thickness between 1 and 7 microns, with the first sample being a lightly-doped, 2.5-micron-thick film with a NEA emitting surface (as indicated by yield measurements of ~20). For beam energies above 13 keV, the transmitted intensity is sharply peaked ~0.60 eV above the emission onset with a FWHM of ~0.60 eV. At constant beam energy (or current), the peak width, position, and emission onset remain constant as the beam current (or energy) is increased, and the peak is very similar to that obtained in reflection measurements. At beam energies below 13 keV, the transmission peak is much broader and less intense. It is possible that the light B doping impacts the transport of electrons to the front surface since a sharp peak was observed at all energies in a previous study of a more conductive 2-micron-thick film. Our ongoing studies continue to examine the role of doping and film thickness on the transmission properties of diamond films.

9:40am **TF-FrM5 Influence of Nitrogen and Temperature on the Deposition of Fluorinated Amorphous Carbon Films***, **L. Valentini**, E. Braca, J. Kenny,* Universita di Perugia, Italy*; R.M. Montereali,* Dip. Innovazione ENEA C.R. Frascati, Italy*; L. Lozzi, S. Santucci,* Universita dell'Aquila, Italy

Plasma deposited hydrogenated amorphous (a-C:H) carbon and fluorinated amorphous carbon films (a-C:H:F) are among the potential candidates considered for the low dielectric constant (k) interconnects. Incorporation of the low-k materials in ULSI integrated structures imposes a lot of requirements to be satisfied, among them stability at the processing temperature of 400Â°C. As deposited a-C:H:F films may be thermally stabilised, in terms of dimensional stability and material loss, by nitrogen incorporation. In this work the effect of nitrogen addition on the properties of a-C:H:F films produced by radio-frequency plasma enhanced chemical vapor deposition has been investigated. The films were studied as a function of nitrogen content and deposition temperature. The structural and optical properties were investigated by x-ray photoelectron spectroscopy (XPS), Raman spectroscopy, UV-VIS transmittance and ellipsometry measurements. The dependence of both fluorine and nitrogen incorporation in the carbon matrix on deposition temperature has been analysed. It was found that the main effect of progressive nitrogen incorporation is a decrease of transmittance and optical band gap of the samples grown at room temperature and at 400Â°C. Raman spectra evidence that for films deposited at 400Â°C a sudden loss of sp3 carbon bonding occurs. In particular, at fixed plasma composition the decrease of the optical band gap is interpreted as a clustering of the existing sp2 carbon sites. The ellipsometry characterization indicates that nitrogen incorporation for the room temperature deposited samples induces an increase of the refractive index and suggested that carrying out a deposition at 400Â°C the films undergo a reduction of the refractive index; this has been correlated to changes in the graphitic cluster size of the network. In particular the increase in the deposition temperature produces an increase in the size of the graphitic clusters.

10:00am **TF-FrM6 Investigation of Nitrogen Bonding in Amorphous Carbon Nitride***, **W.J. Gammon,*** College of William & Mary*; O. Kraft,* Max-Planck-Institut für Metallforschung, Germany*; R.L. Vold, G. Houtson, A.S. Reilly, B.C. Holloway,* College of William & Mary

Previous x-ray photoelectron spectroscopy (XPS) work has shown that the N(1s) spectra of highly elastic amorphous carbon nitride (CN@sub x@) can be resolved into two peaks positioned at ~ 398.5 and 401 eV.@footnote 1@ Furthermore, the exact location and intensity of the two peaks is directly correlated to the mechanical properties of the film.@footnote 2@ Based on XPS data and theoretical calculations, earlier work suggests that the N(1s) peak at 398.5 eV in hard and elastic CN@sub x@, is due to nitrogen bonded to sp@super 3@ hybridized carbon.@footnote 2@ @super -@ @footnote 3@ This interpretation supports the phenomenological model that the mechanical properties of hard CN@sub x@ are due to the cross-linking of graphitic planes through sp@super 3@

bonded carbon.@footnote 2@ However, we present XPS data that suggest the low binding energy N(1s) peak may be due to sp@super 2@ coordinated nitrogen to carbon in an aromatic ring. Also, our data show that the N(1s) peak exhibits bonding over the whole range of possible hybridization. In fact, XPS is not sensitive enough to make unambiguous peak assignments in CN@sub x@, and XPS exhibits no resolvable chemical shift between sp@super 2@ and sp@super 3@ bonded carbon to carbon. However, nuclear magnetic resonance spectroscopy (NMR) provides better discrimination to these bonding types. Therefore, the purpose of this study is to clarify the dependence of chemical bonding on mechanical properties by using NMR data to remove the ambiguity of proposed XPS peak assignments. In this work, we present @super 13@C and @super 15@N NMR, XPS, and FTIR data on CN@sub x@. These films were deposited on a heated Si(001) substrate by DC magnetron sputtering, and nanoindentation was used to quantify the mechanical properties. NMR results are shown for both the hard and elastic phase (deposited at temperatures > 300 @super o@ C) and mechanically poor phase (deposited at ambient temperature). In addition, computational models will be developed concurrently from experimental data to investigate the stability of carbon/nitrogen structures. @FootnoteText@ @footnote 1@ B.C. Holloway, O. Kraft, D.K. Shuh, M.A. Kelley, W.D. Nix, P. Pianetta, and S. Hagström, Appl. Phys. Lett., 74, 3290 (1999). @footnote 2@ N. Hellgren, M.P. Johansson, E. Broitman, L. Hultman, and J. Sundren, Phys. Rev. B, 59, 5162, (1999). @footnote 3@ Å. Johansson and S. Stafström, J. Che. Phys., 111, 3203, (1999).

10:20am **TF-FrM7 Structural and Physical Properties of Carbon Nitride Films with High Nitrogen Content Synthesized by Reactive Pulsed Laser Deposition***, **J.P. Zhao**, Z.Y. Chen, T. Yano, T. Ooie,* National Institute of Advanced Industrial Science and Technology, Japan

Carbon nitride films with high nitrogen content were prepared by reactive pulsed laser deposition in nitrogen atmosphere. The fourth harmonic from a Q-switch Nd:YAG laser with wavelength of 266 nm and pulse duration of 10 ns was focused onto a high purity (99.99%) highly-oriented-pyrolytic-graphite (HOPG) target for producing carbon plume. The laser was pulsed at a rate of 10 Hz. Laser fluence was kept around 12.7 J/cm@super 2@ during deposition. Base pressure of the deposition chamber was lower than 3x10@super -7@ Torr. Nitrogen gas of 99.999% purity was admitted into the chamber during deposition, with pressure varying from 0.1 to 20.0 Torr. It was found that the nitrogen content in the films first increases with increasing the nitrogen pressure, reaches a maximum of 46 at. % at 5.0 Torr, and then decreases to 37 at.% at 20.0 Torr. The almost pure carbon nitride films were systematically characterized by using X-ray photoelectron spectroscopy (XPS) concerning on the core level and valence band structures. With adding the nitrogen incorporation, both the binding energy and peak intensity of the core level and valence band spectra vary systematically as a function of nitrogen content in the films. Structural and physical properties were also studied by using glancing angle X-ray diffractionmeter (XRD), atomic force microscopy (AFM), Fourier transform infrared (FTIR) spectroscopy, micro-Raman spectroscopy, and UV-visible spectrophotometer. Some fingerprint information that show the role of nitrogen in controlling the electronic structure and physical properties of carbon nitride film were found based on these studies.

10:40am **TF-FrM8 Structure and Properties of Carbon Nitride Thin Films Synthesized by Nitrogen-Ion-BeamAssisted Pulsed Laser Ablation***, **Z.Y. Chen**, J.P. Zhao, T. Yano, T. Ooie,* National Institute of Advanced Industrial Science and Technology, Japan

Carbon nitride films were deposited by pulsed KrF excimer laser ablation of graphite with assistance of low energy nitrogen-ion-beam bombardment. The nitrogen to carbon ratio, bonding state, microstructure, surface morphology, and electrical property of the deposited carbon nitride films were characterized by x-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, micro-Raman spectroscopy, atomic force microscopy (AFM), and four-probe resistance. The irradiation effect of the nitrogen ion beam with various ion currents on the synthesis of carbon nitride films was investigated. XPS and FTIR analyses indicated that the bonding state between the carbon and nitrogen in the deposited films was significantly influenced by the nitrogen irradiation with different ion currents during deposition. The carbon-nitrogen bonding of C-N and C=N was observed in the films. High nitrogen ion current was proposed to promote the desired sp@super 3@-hybridized carbon and the C@sub 3@N@sub 4@ phase. In addition, the tribological properties of the carbon nitride films deposited on TiN coated stainless steel substrates were also studied in both dry and oil environments, which exhibited a low friction coefficient and low wear compared to hard TiN film and commercial stainless steel.

11:00am **TF-FrM9 On the Preparation of Silicon Carbonitride Compounds***, **H. Lutz**, M. Bruns,* Forschungszentrum Karlsruhe, Germany*; E. Theodossiu, H. Baumann,* Universitaet Frankfurt/Main, Germany

Carbonitride as well as Silicon Carbonitride thin films have been the subject of great interest in recent years due to the expected improvement of surface properties for a lot of applications. Various precursor based techniques have been employed to synthezise the pure materials. However, most of these efforts result in amorphous films or tiny crystals embedded in amorphous matrices of deficient nitrogen content and considerable hydrogen and oxygen content, respectively. Very promising approaches to Si-C-N synthesis are R.F. magnetron sputtering and ion implantation providing tailored stoichiometries at high purity. Silicon carbonitrides were reactively sputtered using @super 15@N enriched N@sub 2@/Ar sputter gas and co-sputter targets with different Si/C areas resulting in defined and reproducible Si/C ratios at constant nitrogen concentrations. Alternatively, surface modification by sequential high fluence implantation of C and N ions into silicon allows for tuning the atomic fraction of all elements over a wide range. Both techniques enable us to synthezise ternary systems of more than 52 at.% nitrogen content, which are stable up to 1000°C. @paragraph@ The chemical composition of the Si-C-N films was characterized by means of X-ray photoelectron spectroscopy. In case of the buried implanted layers chemical binding states were attainable after sputter etching using 300 eV Ar ions of a projected range minimized to a negligible part of the XPS information depth. In addition, Auger electron spectroscopy, FTIR spectroscopy, and Raman spectroscopy were used to achieve a comprehensive characterization. For quantification XPS and AES data were calibrated with absolute concentration values from non-Rutherford backscattering spectrometry. Furthermore, both preparation techniques have the advantage that @super 15@N and @super 13@C isotopes can be introduced into the layers enabling non-destructive nuclear reaction analysis for depth profiling.

11:20am **TF-FrM10 The Investigation of Homogeneity of a-SiC:H Thin Films***, B.G. Budaguan,* Moscow Inst. of Electronic Technology, Russian Federation, Russia*; **A.A. Sherchenkov**, E.I. Artemov,* Moscow Inst. of Electronic Technology, Russian Federation

Hydrogenated amorphous silicon-carbon alloy (a-SiC:H)is an important material for device applications because of the possibility to control the optical bandgap by changing the carbon concentration. The physical properties and stability of a-SiC:H as well as device quality strongly depend on material's structural properties and, particularly, on its structural homogeneity. In this paper we determine the local chemical environment of the Si-H bond and the forms of carbon incorporation by analysing with use of chemical induction model the dependence of the Si-H stretching frequency shift on the alloy composition r=[C]/[Si]. a-SiC:H thin films were prepared by decomposition in the low frequency (55 kHz) glow-discharge plasma the gases mixture of silane and methane with varying methane fraction at substrate temperature of 320°C. Si and C atoms can be backbonded to Si-H bond in four possible ways to form HSiSi@sub 3-n@C@sub n@ configurations with n=0-3. So we decomposed the IR absorption band between 1840 and 2300 cm@super -1@ attributed to the Si-H stretching vibrations in monohydride SiH group into four subbands with Gauss distributions. Using the chemical induction model we calculated the dependencies of frequencies for each of four peaks both on the local environments of the Si-H group, and on the medium. In order to estimate the validity of frequency evaluations we calculated the probabilities of HSiSi@sub 3-n@C@sub n@ structures as the functions of r assuming the homogeneous film and random bonding. We observed two slopes on the dependence of the Si-H stretching mode peak position on r. At r0.16 the inhomogeneity in medium is due to carbon clustering in the forms of mentioned above structures with n=2 3. The influence of structural configurations on optical properties was discussed.

Vacuum Science & Technology
Room 125 - Session VST+MS-FrM
Semiconductor & Functional Coating Systems & Processes

Moderator: J. Noonan, Argonne National Laboratory

8:20am **VST+MS-FrM1 Advances in Semiconductor Physical Vapor Deposition Equipment; Vacuum, System Architecture, and PVD Source Technology***, **D.J. Harra**,* Novellus Systems, Inc. **INVITED**

Recent advances in physical vapor deposition (PVD) equipment have enabled 0.13-micron and smaller semiconductor device geometries, while also supporting technology transitions from traditional aluminum interconnects to copper, as well as wafer size transitions from 200 mm to 300 mm. Evolutions in PVD system architecture and wafer flow that enable high productivity, as well as incorporation of new technologies such as ionized PVD, and CVD are discussed. In addition, recent developments in sputter source technology will also be discussed. Selected process applications and results are presented to illustrate PVD extendibility to future technology nodes.

9:00am **VST+MS-FrM3 Enhancement of Dielectric CVD Remote Clean Competitiveness Through Improved Gas Utilization***, **T. Nowak**, T. Tanaka, B.H. Kim, M. Seamons, K.B. Jung,* Applied Materials, Inc.

Remote plasma cleaning of dielectric CVD process chambers has been shown to virtually eliminate emission of global warming gases, increase chamber throughput, and increase the lifetime of process chamber hardware. Nitrogen trifluoride (NF@sub 3@) is the principal precursor used in remote plasma cleaning applications because of the ease with which it is dissociated and the high atomic fluorine content achievable at the exit of the remote plasma source. The relatively high cost of NF@sub 3@, however, makes improvement of gas utilization during the remote clean and development of alternative chemistries critical to enhancing the competitiveness of this green manufacturing process. Building on earlier experimental work, we have developed process models and designed experiments to investigate fluorine radical loss mechanisms and utilization efficiencies within parallel plate plasma CVD reactors. Modeling was based on an iterative solution of a one-dimensional flow network with variable gas composition to model transport and recombination losses from the remote plasma source to the process chamber. Calculated values of the atomic fluorine concentration in the process chamber were verified experimentally by measuring etch rates on SiO@sub 2@ wafers. Using the results of the simulation we were able to develop more efficient remote clean processes that, depending on residue to be cleaned, reduce NF@sub 3@ consumption by up to 60% without impacting chamber throughput. In addition, we investigated C@sub 3@F@sub 8@ as an alternative feed gas for the remote clean. Experiments showed that cleaning rates on the order of 80% of NF@sub 3@-based cleans were achievable using C@sub 3@F@sub 8@.

9:20am **VST+MS-FrM4 Vacuum System Architecture for Disk and Flat Panel Production Tools***, J.L. Hughes, **J. Busch**,* Intevac Inc. **INVITED**

Production tools using high vacuum environments are increasingly used by industry, with their requirements growing more difficult. Two such applications are flat panel displays and magnetic hard disks. The flat panel uses up to 1.2 x 1.6 meter rectangular substrates of 1.1 mm thick glass, while hard disks are typically 95 mm circular aluminum. The methods for thin film deposition by sputtering for the two systems varies greatly for the two applications. The same thing is true for substrate transport. But some methods and principals remain the same in either type of production. Vacuum levels run from 1.0E-08 Torr for high vacuum to sputtering pressures of 5.0E-03 Torr. This article looks at two specific examples of vacuum system architecture and draws out the specifics of difference and samenesss between the two.

10:00am **VST+MS-FrM6 Disassembling and Materials Recovering Process of Zinc-Carbon battery by Vacuum Aided Recycling Systems Technology***, **Y. Saotome**,* Gunma University, Japan*; Y. Nakazawa,* Kokushikan University, Japan*; Y. Yamada,* Nagata Seiki Co., Ltd., Japan

Every material has its own vapor pressure and the principle of VARS Tech. is based on sorting and recovering a specific material from the midst of other combined products through evaporation in a vacuum and the use of different evaporation temperatures for each material.@footnote 1@ In the present paper, VARS Tech. has been applied to the recycling of used batteries. Zinc-Carbon battery R20PU was selected as a specimen and was heated by radiation through vacuum vessel wall made of glass. The resulting relationship between vacuum pressure, reduction in mass and the temperature during heating indicates the occurrence of some evaporation. For the analyses of these complex phenomena, similar experiments were carried out on each component and material of the battery. As a result, at the temperature of about 450K, PVC insulation ring at the top of the battery becomes warped and then water(solution) is evaporated from the inside of battery. From the aspect of recycling process, softening and decomposition phenomenon of PVC insulation ring is correspond to the beginning of disassembling of battery as an assembled product. Actually, disassembling process is accelerated by the evaporation of ZnCl@sub 2@ and can-zinc above about 700K. After the vacuum thermal cycle, the specimen is disassembled and comes to parts such as jacket-metal, some plate metals, an electrode-carbon and positive reactant in powder state. As shown above, the vacuum-aided recycling method is a process that consists of disassembling, sorting, and recovering materials. As shown above, vacuum aided recycling technology has superior characteristics as a restoration systems technology of EcoFactory. As shown above, vacuum aided recycling technology has superior characteristics as a restoration systems technology of EcoFactory. @FootnoteText@ @footnote 1@ Y.Saotome, Y.Nakazawa and Y.Yamada, Vacuum, 53(1999), 101-104.

10:40am **VST+MS-FrM8 The Foundations of Vacuum Coating Technologies***, **D.M. Mattox**,* Management Plus, Inc.

Vacuum coatings processes use a vacuum environment and an atomic or molecular vapor source to deposit thin films and coatings. The vacuum environment is used not only to reduce gas particle density but also to limit gaseous contamination, establish partial pressures of gases and control gas flow. Electric power is used to thermally vaporize material, thermally decompose vapors, activate reactive species, generate plasmas and accelerate ions. This paper will trace the development of vacuum technology from the piston water pumps of the Roman Empire, the development of electric power from frictional electricity machines and the electrolytic cell, and the development of deposition techniques based on thermal evaporation, sputtering, arc vaporization, laser ablation and chemical vapor precursors. Both patent and technical literature will be cited as to the first reports on phenomena and processes and the beginnings of sustained applications of various vacuum-coating processes. Several areas of uncertainty will be described and discussed. Often these uncertainties are due to problems with terminology or to the differing nature of patent and technical literature. Several areas where original ("pioneering") work is commonly attributed to an inappropriate individual(s) will be discussed.

11:00am **VST+MS-FrM9 Downstream Effluent Management Subsystems for Semiconductor Manufacturing Processes***, **Y. Gu**,* MKS Instruments, Inc. **INVITED**

Smaller geometry and larger wafer size are the major trends for today's semiconductor device manufacturing industry in order to attain higher throughput and better device performance. At the same time, tool uptime and process yield become more important as they are closely related to the fab throughput. Significant efforts have been spent on improving the process throughput by employing advanced tools, new process chemistries and more efficient in-situ cleaning steps. However, it was found that the tool usage is often reduced because of existing downstream problems. In addition, particle levels on wafer surface are also related to the cleanness of the pump line. These problems are even getting worse because of the use of more reactive precursors, which are intended to reduce the process temperature and increase the deposition rate. The most common processes which are experiencing significant downstream problems are silicon nitride LPCVD, TEOS LPCVD, Aluminum etch, tungsten CVD process, silicon Epi, and variety of other processes. These problems can be caused by physical sublimation of the condensable by-products, or the complex chemical reactions between unreacted precursors, by-products, and/or the vapor backstreaming from the scrubber. Different techniques are required to manage these effluent problems because of their different mechanism. In addition, a systematic solution is often required in order to prevent creating a problem. Several downstream effluent management subsystems developed at MKS Instruments Inc. will be discussed in this talk. They have been proven very effective to improve semiconductor manufacturing process uptime and yield.

Vacuum Science & Technology
Room 132 - Session VST-FrM

Accelerators Technology, Fusion Machines & Gravitational Wave Detectors

Moderator: R. Reid, Daresbury Lab, U.K.

8:20am **VST-FrM1 RHIC Commissioning and First Results***, **S. Ozaki**,* Brookhaven National Laboratory **INVITED**

The Relativistic Heavy Ion Collider (RHIC) at Brookhaven National Laboratory is the U.S. Department of Energy’s flagship research facility for the nuclear physics program. With the capability to collide ions as heavy as Au at the center-of-mass energy of 200 x A GeV, where A is the atomic mass of the ion, the primary objective of RHIC is to create states of nuclear matter at an extreme high temperature and density. We believe that such states of matter existed for a fleeting moment, shortly after the creation of the universe, as we know it know, by so called "Big Bang". The construction of the collider, consisting of two superconducting magnet rings of 3.8 km in circumference, was completed as scheduled during 1999. Following the initial commissioning of the collider in the same year, collisions of Au ions were achieved during the subsequent commissioning run in the year 2000, first at the collision energy of 66 GeV per nucleon in the Au ion on June 12 and later at 132 GeV per nucleon. By the end of that year's run, the luminosity of the collisions reached more than 10% of the design value. All four detectors of RHIC, i.e., BRAHMS, PHENIX, PHOBOS, and STAR, were also commissioned, using these collision events and collected a significant amount of data before the end of the run. An overview of the RHIC facility construction project, commissioning of the facility, and the first physics results at the new frontier of nuclear matter research will be presented. @FootnoteText@ @ Brookhaven National Laboratory BSA Upton, Long Island, New York 11973 Work Performed Under The Auspices Of The U.S. Department Of Energy Under Contract # DE-AC02-98CH10886 UNITED STATES DEPARTMENT OF ENERGY

9:20am **VST-FrM4 The SNS Accumulator Ring Vacuum Systems@footnote *@***, P. He,* ***H.C. Hseuh,*** Brookhaven National Laboratory*; M. Mapes,* Brookhaven National Laboratory, usa*; L. Smart, R. Todd, D. Weiss,* Brookhaven National Laboratory

Brookhaven is undertaking the design, construction and commissioning of the accumulator ring and the transport lines for the 1-GeV Spallation Neutron Source. To limit the residual gas ionization by the proton beam, the operating pressure of the ring vacuum system is 10@super -9@ Torr. The inner surface of the accumulator ring vacuum chambers will be coated with titanium nitride to minimize the secondary electron yields. The vacuum requirements and the layout of the vacuum systems will be discussed. The design of the vacuum chambers, vacuum pumps, and quick disconnect flanges and the development of vacuum instrument and control system will also be presented. @FootnoteText@ @footnote *@Work performed under the auspices of the U.S. Department of Energy.

10:00am **VST-FrM6 Photon Induced Desorption Studies on Sputter-deposited Getter Layers***,* ***V. Baglin****, C. Benvenuti, P. Chiggiato, P. Costa Pinto, N. Hilleret, A. Rossi,* CERN, Switzerland

Two vacuum chambers coated with a thin film of Ti-Zr-V non evaporable getter have been exposed, under normal incidence, to the synchrotron radiation emitted by the bending magnets of EPA (critical energy 194 eV). The coatings were produced using different coating parameters and the configuration of the experimental set-up was conceived to minimize the background signal and to allow the gas desorption and the pumping processes to be disentangled. The measurements have been repeated after heating the coated chambers at progressively higher temperatures up to the complete getter activation. The study has been also extended to cover the influence of the pumped gas load on the desorption yield, providing a quantitative evaluation under the various experimental conditions. The results are presented and compared with those obtained from a bare stainless steel vacuum chamber.

10:20am **VST-FrM7 Design of the NIF Spatial Filter Vacuum System***,* ***J.D. Hitchcock****, J.M. Bowers, P.J. Densley, C.E. Karlsen, H.G. Patton, J.R. Reed,* Lawrence Livermore National Laboratory*; J.W. Weed,* Sandia National Laboratories

The National Ignition Facility (NIF) is a Department of Energy inertial confinement fusion facility. The goal of the facility is to achieve fusion ignition and modest energy gain in the laboratory. The multi billion dollar NIF project is responsible for t he design and construction of the 192 beam, 1.8MJ laser necessary to meet this goal. The NIF is a national project with participation by LLNL, LANL, SNL, URLLE and numerous industrial partners. The NIF spatial filter vacuum system will provide 10@SUPER-4@ torr or less to each of 48 individually pumped volumes for a total of 3.3 x 10@SUPER6@ liters. These volumes involve 2300 tons of stainless steel vessels and connecting beam tubes. The spatial filters are clean room rated to MIL STD 1246C level 83 - A/1 0 and the total internal surface area, excluding internal components, is 22,500 sq. m. The system design has been completed and the vessels are installed in the NIF laser bays. Installation of the beam tubes and vacuum pumping equipment is in progress w it h initial operations beginning in July 2002. The pumping system consists of magnetically levitated turbo molecular drag pumps and redundant, "dry" vessel roughing and turbo backing pump skids. Controls, auto sequencing, data archiving, trending, inter l ock s and alarm functions will be provided by programmable logic controllers. Gauging includes total pressure with provisions for partial pressure and leak detection measurements. The hardware, instrumentation, design criteria and performance goals will be described. This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

10:40am **VST-FrM8 Direct Measurement of Residual Gas Effect on the Sensitivity in TAMA300***,* ***R. Takahashi,*** National Astronomical Observatory of Japan, Japan*; Y. Saito,* High Energy Accelerator Research Organization, Japan*; M. Ando,* The University of Tokyo, Japan*; K. Arai, M. Fukushima, G. Heinzel, S. Kawamura, D. Tatsumi, T. Yamazaki,* National Astronomical Observatory of Japan*; S. Moriwaki,* The University of Tokyo, Japan

A laser interferometer gravitational wave detector requires an ultra-high vacuum in the ducts which the laser beams pass through. TAMA300, involving two 300 m-long vacuum ducts, is kept in 2x10@super -6@ Pa of vacuum pressure so as to reduce scattering-effects due to residual gas molecules. The sensitivity attained so far is 2x10@super -18@ m/rtHz around 1 kHz. By introducing a Xe-gas into the entire system of TAMA300, we directly observed the residual-gas effect on the sensitivity. It is found that the Xe-gas pressure of 6x10@super -2@ Pa induces an increase in the mirror displacement noise of 3x10@super -18@ m/rtHz. This noise level is consistent with a calculated optical fluctuation of the laser beam due to residual-gas scattering.

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