Sunday Afternoon, October 30, 2005

Biomaterials Plenary
Room 312 - Session BP-SuA

Biomaterials Interfaces Plenary Session

Moderator: G.J. Leggett, University of Sheffield, UK

3:00pm **BP-SuA1 Bio-Surfaces: Frontiers and Possibilities***, B.D. Ratner,* University of Washington Engineered Biomaterials (UWEB) **INVITED**

What does a real bio-surface look like? Two compelling examples in nature are (1) the basement membrane structures upon which endothelial cells and epithelial cells are adhered to in living creatures and (2) the surface of living cells. The characteristics of these real bio-surfaces are the presence of multiple recognition molecules that are oriented appropriately and conformationally stabilized, considerable molecular mobility used to turn on and off signals, an appropriate mechanical environment, options for repair of degraded components and inhibition of non-specific interactions. How might we, as "biointerface scientists," emulate all or part of the obvious functionality of such complex biosurfaces? This will be the focus of this lecture. The following subjects will be discussed and examples presented: inhibition of non-specific interactions; controlled surface molecular mobility; artificial surfaces with extracellular matrix components; protein orientation for signal delivery.

3:40pm **BP-SuA3 Observing Membrane-Embedded Biological Nanomachines Using the AFM***, D. Fotiadis, P.N.T.L. Frederix, H. Remigy,* ***A. Engel,*** M.E. Mueller Institute, Switzerland **INVITED**

Membrane proteins are membrane-embedded nanomachines at cellular interfaces that fulfill key functions such as energy conversion, solute transport, secretion, and signal transduction. The lack of structural information is related to the instability of membrane proteins in a detergent-solubilized state, making the growth of three-dimensional (3-D) crystals difficult. Direct observation of native membranes using the atomic force microscope (AFM) is therefore of great interest. Alternatively, two-dimensional (2-D) crystals of purified membrane proteins reconstituted in the presence of lipids provides a close to native environment and allows the structure and function of membrane proteins to be assessed. To this end, we use electron crystallography, which provides 3-D information at the atomic level. AFM allows the surface of membrane proteins to be studied at sub-nm resolution, providing information about their conformational variability that cannot be assessed by crystallographic methods. In addition, atomic force microscopy is the tool of choice to study the conformation and molecular arrangements of proteins in native membranes.

4:20pm **BP-SuA5 New Advances in Optical Imaging of Living Cells***, X.S. Xie,* Harvard University **INVITED**

The combination of new probes with advanced microscopy allows real time observation of biological processes in living cells at an unprecedented level. In particular, semiconductor quantum dots, coupled with high speed confocal microscopy, make it possible to resolve individual steps of molecular motors with nanometer spatial resolution and millisecond time resolution. By developing a new reporter protein, we are able to observe stochastic events of gene expression, and detecte protein being generated one molecule at a time in E. Coli cells. Advances in Coherent Anti-Stokes Raman Scattering (CARS) microscopy enable us to visualize living cells and tissues based on vibrational spectroscopy without fluorescence labels.

Topical Conference on Renewable and Alternate Energy
Room 304 - Session EN-SuA

Renewable and Alternate Energy

Moderators: R. Ahrenkiel, University of Denver, G. Parsons, North Carolina State University

3:00pm **EN-SuA1 Scientific Challenges in Sustainable Energy Technology***,* ***N.S. Lewis,*** California Institute of Technology **INVITED**

This presentation will describe and evaluate the challenges, both technical, political, and economic, involved with widespread adoption of renewable energy technologies. First, we estimate the available fossil fuel resources and reserves based on data from the World Energy Assessment and World Energy Council. In conjunction with the current and projected global primary power production rates, we then estimate the remaining years of supply of oil, gas, and coal for use in primary power production. We then compare the price per unit of energy of these sources to those of renewable energy technologies (wind, solar thermal, solar electric, biomass, hydroelectric, and geothermal) to evaluate the degree to which supply/demand forces stimulate a transition to renewable energy technologies in the next 20-50 years. Secondly, we evaluate the greenhouse gas buildup limitations on carbon-based power consumption as an unpriced externality to fossil-fuel consumption, considering global population growth, increased global gross domestic product, and increased energy efficiency per unit of globally averaged GDP, as produced by the Intergovernmental Panel on Climate Change (IPCC). A greenhouse gas constraint on total carbon emissions, in conjunction with global population growth, is projected to drive the demand for carbon-free power well beyond that produced by conventional supply/demand pricing tradeoffs, at potentially daunting levels relative to current renewable energy demand levels. Thirdly, we evaluate the level and timescale of R&D investment that is needed to produce the required quantity of carbon-free power by the 2050 timeframe, to support the expected global energy demand for carbon-free power. Fourth, we evaluate the energy potential of various renewable energy resources to ascertain which resources are adequately available globally to support the projected global carbon-free energy demand requirements. Fifth, we evaluate the challenges to the chemical sciences to enable the cost-effective production of carbon-free power on the needed scale by the 2050 timeframe. Finally, we discuss the effects of a change in primary power technology on the energy supply infrastructure and discuss the impact of such a change on the modes of energy consumption by the energy consumer and additional demands on the chemical sciences to support such a transition in energy supply.

3:40pm **EN-SuA3 Our Solar Power Future: The U.S. PV Industry Roadmap for 2030 and Beyond***,* ***A.M. Barnett,*** University of Delaware*; R. Resch,* Solar Energy Industries Association **INVITED**

The next 10 years are critical for worldwide solar power development. Actions by industry and government will determine whether solar power is catapulted to a new level and whether the United States will regain its position at the forefront of solar power development. Investment decisions over the next decade for research, new manufacturing, and creating new markets will determine where solar power will thrive-and where it will merely survive. Solar power can provide great value in residential and commercial grid-connected applications, for individual consumers and businesses, as well as for utilities and the communities they serve. Our goals for 2030 are solar power system costs of $2.33 per watt, solar electricity prices of 3.8 cents per kilowatt-hour (kWh) delivered to the customer, installed solar power generation of 200 gigawatts (GW), and direct employment of 260,000 people.

4:20pm **EN-SuA5 Hydrogen and Chemicals from Fossil and Renewable Fuels by Autothermal Reforming***,* ***L.D. Schmidt,*** University of Minnesota **INVITED**

Autothermal reactors have great promise for hydrogen and chemicals production because they have reactor residence times of 10-3 seconds and require very simple reactors. We describe the production of hydrogen and olefins from fossil fuels from methane to diesel and from renewable fuels such as ethanol and biodiesel in millisecond reactors. For successful vaporization and mixing of heavy fuels the use of fuel injectors for rapid vaporization and mixing is essential to suppress flames and carbon formation. For ethanol to hydrogen we obtain 80% selectivity to hydrogen at nearly 100% conversion of ethanol and oxygen for an ethanol-air feed. By adding water we obtain 110% (H2 from ethanol and water) in a single stage reactor and 130% H2 selectivity in a staged reactor where a cooler section undergoes the water gas shift reaction. For biodiesel (the methyl ester of C18 fatty acids from soy oil), we can obtain 80% H2 selectivity at C/O=0.8 and 80% selectivity to olefins at C/O=1.5. At higher C/O ratios the ester linkage also survives to produce olefinic esters. Modeling with detailed surface and homogeneous chemistry is used to simulate and understand these processes.

5:00pm **EN-SuA7 Fuel Cells from the Viewpoint of a Skeptical Optimist***,* ***T. Zawodzinski,*** Case Western Reserve University **INVITED**

Fuel cells have been the subject of hype and backlash of late. The hype took various forms, including the 'We'll have a product next year' variety as well as inflated estimates system efficiency, simplicity, etc. Hopes have been dashed because of failure to adequately anticipate the difficulty of some technical and practical problems and from the short duration over which present-day configurations have been tested. The backlash has evolved from reaction to not meeting promises as well as from the realization of the aforementioned problems. Also, fuel cells are linked in many minds to the Hydrogen Economy, which has its own set of detractors. After reviewing these promises and pitfalls, this talk will discuss the current state of development of fuel cells, highlighting technical state of the art. Significant achievements and substantial activities to address some of the major challenges posed by the combination of cost, reliability and performance/functionality factors will be highlighted. By presenting a realistic assessment of these aspects, we hope to leave people with 'reasons to believe' in the promise of fuel cell technology in some applications

Applied Surface Science
Room 206 - Session AS+BI+NS-MoM

Nanoscale Analysis: Biomaterial and Other Applications

Moderator: A.M. Belu, Medtronic, Inc.

8:20am **AS+BI+NS-MoM1 The Development of NSOM for Live Cell Applications*, R.C. Dunn,* *O. Mooren,* University of Kansas **INVITED**

Near-field scanning optical microscopy (NSOM) is a scanning probe technique that enables optical measurements to be conducted with nanometric spatial resolution. This technique offers single molecule detection limits, high spatial resolution, and simultaneous force and optical mapping of sample properties. As such, it has found applications in many areas including the study of thin films, polymers, and solid-state materials. Perhaps its greatest potential, however, lies in the biological sciences, where fluorescence techniques are well developed for tagging specific proteins or structures or following dynamic processes such as calcium signaling. To date, NSOM measurements on viable cells remains problematic due to the forces involved in maintaining the tip close to the sample. Our laboratory has been actively developing new methods for conducting NSOM measurements that are amenable with soft and fragile samples such as living cells. We recently reported a new NSOM tip design built around a conventional atomic force microscopy tip that can be used to make high resolution fluorescence measurements on living cells. The development of these techniques and their application to the study of lipid rafts and nuclear pore complexes in the nuclear envelope will be discussed.

9:00am **AS+BI+NS-MoM3 Local Mobility in Membranes: Atomic Force Microscopy and Fluorescence Correlation Spectroscopy*, A.R. Burns,*** *D.J. Frankel,* Sandia National Laboratories

The lateral organization and dynamics of lipids and proteins in membranes are critical to cellular signaling processes. Fluorescence imaging and atomic force microscopy (AFM) are both effective ways to map the location and structure of membrane components and domains (e.g., lipid rafts) in supported membranes. Since dynamical processes like translational diffusion of lipids and proteins are dependent on the local membrane structure and molecular interactions, it would be advantageous to correlate dynamics with detailed topography mapped out with AFM. We do this by performing fluorescence correlation spectroscopy (FCS) at specific sites imaged by simultaneous AFM and submicron confocal fluorescence microscopy. We have thus examined the relative partitioning and diffusion coefficients for both tail and head labeled GM1 ganglioside, as well as for head and tail labeled phospholipids, in phase separated domains. Our results indicate significant mobility changes in the micron-scale domains due to differences in lipid packing and ordering. We also observe a large reduction in the mobility of GM1 when bound to cholera toxin B fragments. The effects of membrane proteins will be discussed as well. This research was supported in part by the Division of Materials Science and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy under Contract DE-AC04-94AL85000.

9:20am **AS+BI+NS-MoM4 Molecular Orientation Imaging with sub 10-nm Resolution by Vector Piezoresponse Force Microscopy*, B.J. Rodriguez,*** North Carolina State University*; S. Jesse, A.P. Baddorf,* Oak Ridge National Laboratory*; A. Gruverman,* North Carolina State University*; S.V. Kalinin,* Oak Ridge National Laboratory

Functional properties of calcified and connective tissues are determined by the relative ordering and orientation of a relatively small number of biopolymers, such as collagen. Here we present a new approach for local molecular orientation imaging in biological systems by Vector Piezoresponse Force Microscopy (Vector PFM). Vector PFM is capable of determining the local electromechanical activity and orientation in piezoelectric materials with a spatial resolution below 10 nm. The applicability of Vector PFM to biological systems is demonstrated for objects from butterfly wings to bones. Electromechanical characterization of enamel and dentin layers in human tooth is demonstrated. The vector electromechanical response of a bundle of collagen molecules in human tooth dentin has been visualized with 5 nanometer resolution. A method for imaging the local orientation of biomolecules from Vector PFM data has been illustrated using collagen molecules embedded in a hydroxyapatite matrix. As another example, 2D piezoelectric properties and local elasticity of a butterfly wing are measured with nanoscale resolution and interpreted in terms of the relative orientation of chitin molecules in the wing scales. The ubiquitous presence of electro-activity in biopolymers, such as chitin, keratin, collagen, and cellulose, suggests that Vector PFM has exceptional potential for orientation imaging of biological materials on the sub-10 nanometer length scale. Research was sponsored by the U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC and by the National Science Foundation grant DMR-0072998 (AG). Research partially performed as a Eugene P. Wigner Fellow (SVK).

9:40am **AS+BI+NS-MoM5 Nanoscale Raman and Fluorescence Microscopy of Carbon Nanotubes*, A. Hartschuh,*** *H. Qian, A.J. Meixner,* University of Tuebingen, Germany*; N. Anderson, L. Novotny,* University of Rochester **INVITED**

Spectroscopic methods with high spatial resolution are essential for understanding the physical and chemical properties of nanoscale materials including biological proteins, quantum structures and nanocomposite materials. Optical techniques are of special interest because the energy of light quanta is in the range of electronic and vibrational transitions. Advances in near-field optics open up new means to overcome the diffraction limit and extend the range of optical measurements to the length scales of most nanosystems. Recently, a near-field optical technique based on local field enhancement has been demonstrated which allows to perform spectroscopic measurements with 20 nm spatial resolution.@footnote 1,2@ The method makes use of the strongly enhanced electric field close to a sharp metal tip under laser illumination. In this approach the metal tip is held a few nanometers above the sample surface so that a highly localized interaction between the enhanced field and the sample is achieved. Raster scanning the sample then allows for simultaneous optical and topographic imaging. Single-walled carbon nanotubes (SWCNTs) have been the focus of intense interest due to a large variety of potential nanotechnological applications. We demonstrate near-field Raman and fluorescence imaging of the same individual single-walled carbon nanotube and show that a spatial resolution of less than 20 nm can be achieved. The high-resolution capability and chemical specificity of the presented method is used to study local variations in the optical spectra of SWCNTs which would be hidden in farfield measurements. The technique has great potential for becoming a routine tool for the chemical analysis of surfaces at high spatial resolution. @FootnoteText@ @footnote 1@ E. J. Sanchez et. al, Phys. Rev. Lett. 82, 4014 (1999).@footnote 2@ A. Hartschuh et. al, Phys. Rev. Lett. 90, 095503 (2003).

10:20am **AS+BI+NS-MoM7 Scanning Atom Probe Study of Fragmentation of Organic Molecules*, O. Nishikawa,*** *M. Taniguchi,* Kanazawa Institute of Technology, Japan

Fragmentation of two organic molecules, crystal violet [(C@sub25@N@sub3@H@sub30@)@super+@Cl@super-@: 408 amu] and tetra-n-butyl-ammonium hydroxide [N(C@sub4@H@sub9@)@sub4@@super+@OH@super-@: 259 amu], was studied at atomic level by mass analyzing the dissociated fragments with the scanning atom probe (SAP). In the SAP analysis the molecules and their fragments are field evaporated as positive ions and detected one by one. Since the field evaporation is a static process, it does not disorder surface structure breaking atomic bonds by external energy. Accordingly, evaporated positive ions reflect the binding state in the molecules. For example, the radical of polythiophene, SC@sub4@H@sub2@, is field evaporated as doubly charged ions indicating that the atoms forming the radical are strongly bound. A thin layer of crystal violet was deposited on a tungsten substrate. Since the crystal violet is non conductive, the molecules are field evaporated applying a DC high voltage to the tungsten substrate and irradiating the specimen with a pulsed laser beam, 2nd harmonic of YAG laser, 532 nm. Although non-dissociated molecule ions are detected, most molecules are dissociated showing the ions such as C@sub13@H@sub2@, C@sub13@NH@sub4@ and C@sub8@NH@subn@. The detected fragments suggest that no double bonds are broken. When the molecule layer was deposited on a titanium oxide layer, all molecules were dissociated possibly due to the photo-catalytic function of titanium oxide. The most abundant fragment is C@sub4@NH@subn@. The ratio of the number of carbon atoms to that of nitrogen atom was found to be nearly 8:1 as expected. Although the dissociation of tetra-n-butyl-ammonium hydroxide molecules at the boundary with the tungsten substrate is noticeable, the dissociation is insignificant at non-boundary areas. It was also found that hydroxide of the molecules is dissociated and oxygen atoms are bound with tungsten. This may suggest that tungsten also have catalytic function.

10:40am **AS+BI+NS-MoM8 Surface Potential Mapping of DNA-protein Complex at Molecular Level***, **E. Mikamo**, F. Yamada, T. Matsumoto, T. Kawai,* Osaka University, Japan

Atomic force microscopy (AFM) is a valuable method for the study of biomolecules such as DNA, RNA and proteins at real-space. The biomolecules have generally been adsorbed on the insulating substrate as mica to observe by AFM. However, it is very hard to measure the local electric properties of the insulating substrate and the conductive substrate has been commonly used. Recently our group demonstrated the measurement of electric properties of DNA and Au nanoparticles on mica and sapphire substrate. This result encouraged us to measure the complex of biomolecules on the insulating substrate at molecular level. We report here surface potential and capacitance measurement of DNA, protein and DNA-protein complex on the insulating substrate. The experiments are based on frequency mode non-contact AFM (FM-ncAFM). The FM-ncAFM is able to detect the high-sensitive local electrostatic forces and prevent the charge injection caused by tip-sample contact. We observed the surface potential mapping and topographic image simultaneously. The topographic images clearly showed DNA and protein as line and dot structure. The surface potential of corresponded structures is observed as bright contrast. Our results indicate that surface potential of DNA, protein and DNA-protein complex is higher than insulating substrate surface. The potential images resolve the double strand DNA, thin structure less than 2 nm, and protein at single molecular revel. To estimate the capacitance of individual molecules, we measured d(@DELTA@F) per dV images. The measurement of surface potential and capacitance indicate that this technique is able to discriminate the individual molecules on an insulating substrate. This work was supported by grants from the New Energy and Industrial Technology Development Organization (NEDO).

11:00am **AS+BI+NS-MoM9 The Importance of Aberration Corrected SEM and TEM to the Semiconductor Industry***, **A.C. Diebold**,* SEMATECH & AMRC, US*; B. Foran,* ATDF & AMRC*; M.J. Yacaman, B.A. Korgel,* University of Texas & AMRC **INVITED**

Microscopy continues to be a critical need for the semiconductor industry. Feature sizes continue to shrink with logic having a two-year cycle for introduction of each new technology generation. Over the next fifteen years, the gate length of transistors will rapidly shrink to less than 10 nm. The interconnect technology connecting the transistors will keep pace with this size reduction. Research and development needs occur well ahead of manufacturing needs. Thus, there already is a need for microscopy capable of imaging and characterizing the interfaces, film layers and structures for future devices. Recent advances in electron optics technology have corrected for chromatic and spherical aberrations that have long limited resolution in scanning electron microscopy (SEM) and tranmission electron microscopy (TEM). Commercially available advances include monochromators to reduce the energy spread of the electron source and lens correctors to reduce spherical aberration. Resolution of state of the art scanning TEM and High resolution TEM has been proven below 0.1 nm. Aberration correction technology is also now commercially available for SEM and allowing resolution to 0.6 nm. In this paper we discuss the advances in imaging that aberration corrected lenses have enabled along with semiconductor industry applications. We will discuss near-term applications such as the characterization of interfaces in the transistor gate stack and measurement of strain in the transistor channel, and then also discuss long-term research applications such as nanowires and nanodots. Abberation correction will not solve all microscopy problems, and we will discuss specific cases such as sample or analytical limitations that can obviate any benefit of aberration correction technology.

11:40am **AS+BI+NS-MoM11 Scanning Tunneling Microscope Assisted with Inner-Shell Excitation by Hard X-ray Micro-Beam***, **A. Saito**,* Riken Harima Inst., Japan*; J. Maruyama, K. Manabe,* Osaka Univ., Japan*; K. Kitamoto,* Riken Harima Inst., Japan*; K. Takahashi,* Osaka Univ., Japan*; Y. Tanaka,* Riken Harima Inst., Japan*; M. Yabashi, M. Ishii,* Japan Synchrotron Radiation Res. Inst.*; M. Akai-Kasaya,* Osaka Univ., Japan*; S. Shin, T. Ishikawa,* Riken Harima Inst., Japan*; Y. Kuwahara, M. Aono,* Osaka Univ., Japan

A scanning tunneling microscope (STM) system was developed for in-situ experiments under the irradiation of highly brilliant hard x-rays of synchrotron radiation (SR). It appears attractive to excite the core electrons of specific level under the STM observation, because it may enable to analyze the elements or control the local reaction with the spatial resolution of STM. To surmount a small probability of the core-excitation by hard X-rays, SR of the highest brilliance at the SPring-8 was used. To prevail the difficulties produced by the highly brilliant SR (damage around the STM scanner, thermal and electrical noise, and instability of the system such as thermal drift), the beam size was limited to @phi@10 µm. The small beam size serves also to obtain a high signal to noise ratio and high spatial resolution by restraining the electrons emitted from a wide area. The in-situ STM observation was enabled by developing an accurate "three-body (invisible micro-beam, tip-end, and sample surface)" alignment system in ultrahigh vacuum. Despite a noisy condition of SR facility and radiation load around the probe tip, STM images were successfully obtained with atomic resolution. The analysis of the clean Si(111) surface revealed that the thermal expansion affects to the behavior of the tip much strongly than reported in the past reports. Next, the tip-current spectra were obtained on Ge nano-islands on the clean Si(111) surface, by changing the incident photon energy across the Ge absorption edge. A current modification was detected at the absorption edge, with a spatial resolution of the order of 10 nm. This system will serve to observation or manipulation with atomic resolution, which is based on the interaction between the surface atoms and the hard X-ray photons.

Biomaterial Interfaces
Room 313 - Session BI-MoM
BioMaterials and Neutrons (BioMaN) I

Moderator: M. Grunze, Universität Heidelberg, Germany

8:20am **BI-MoM1 Neutron Scattering Tutorial***, **J.K. Zhao**,* Oak Ridge National Laboratory

We will give an introduction to the neutron scattering techniques relevant to the current session. Topics will include Reflectometry, Small Angle Neutron Scattering and Inelastic Scattering. We will briefly describe these methods and introduce various technical terms that will be used by the subsequent talks. These subsequent presentations will concentrate on scientific achievements or potentials of neutron scattering in biomaterials. We will also distribute handouts as technical references during session.

8:40am **BI-MoM2 Compositional Depth Profiles of Biomaterial Interfaces by Specular Neutron Reflection***, **C.F. Majkrzak**, S.K. Krueger, U. Perez-Salas, N.F. Berk,* National Institute of Standards and Technology

We present the results of recent studies which illustrate the power of specular neutron reflectivity and diffraction for determining the compositional depth profiles of thin films and multilayered structures of interest in biology and biotechnology. Research discussed includes: probing the interactions of melittin (a model peptide for antibiotics and membrane proteins) with hybrid bilayers; the structural characterization of a polyelectrolyte/terpolymer/phospholipid sandwich; the orientation of adsorbed biomineralization proteins; and the location of cholesterol within lipid membranes. Using specular neutron reflection from single-repeat lamellar assemblies or diffraction from periodic multilayers as probes, cross sectional composition depth profiles, with spatial resolutions of the order of a nanometer and Angstrom, respectively, can now be obtained. We demonstrate, in the context of the aforementioned work, how the neutron's sensitivity to different isotopes, in particular hydrogen and deuterium, enables detailed structural information -- for example, the water concentration profile across the thickness of a film -- to be revealed through selective substitution in organic materials. We also show how the high transmission of neutrons through inorganic single crystals, e.g., silicon, sapphire, and quartz, allows such crystals to serve as both substrate for the film of interest as well as fronting medium for the incident and specularly reflected neutron beams. This in turn makes it possible to study the film in intimate contact with a fluid reservoir -- which may be, for instance, part of a functioning electrochemical cell. Finally, the uniqueness of a depth profile obtained from neutron reflection data is considered, together with the degree of uncertainty in the density and the spatial resolution.

9:00am **BI-MoM3 Neutron Scattering and Diffraction for Molecular-Scale Characterization of Biomimetic Membranes***, **M. Loesche**,* Johns Hopkins University and CNBT at the NIST Center for Neutron Research

Nanotechnology and molecular bioengineering are making ever deepening inroads into our daily lives. Physicochemical and biotechnological achievements in the design of physiologically active supramolecular assemblies have brought about an urgent need for new means of characterizing them at the molecular and submolecular levels. Because surfaces and interfaces play a pivotal role in this field, surface-sensitive neutron and x-ray scattering techniques have become particularly important for characterization. The CNBT consortium, located at the NCNR, is a biophysics partnership that utilizes neutron scattering, tightly interfaced with MD simulations, for advanced research in membrane biology and biotechnology. A new neutron spectrometer – the Advanced Neutron Reflectometer and Diffractometer, AND/R – has been commissioned which is optimized for surface-sensitive neutron scattering. In this talk, I will discuss current highlights of research performed on the AND/R, including investigations of peptidemembrane interactions and the molecular-scale characterization of model bilayer membranes tethered to solid supports.

9:20am **BI-MoM4 Towards a Deeper Understanding of Protein Resistance: Characterizing Water/Surface and Protein/Surface Interactions by In Situ Neutron Reflectometry*, R. Dahint,*** Universität Heidelberg, Germany*; M. Skoda, F. Schreiber,* Universität Tübingen, Germany*; M. Himmelhaus, M. Grunze,* Universität Heidelberg, Germany

Materials which are resistant towards adsorption of proteins from biological media are of crucial importance in biotechnology and biomedical applications. The most outstanding protein resistant properties are exhibited by surfaces containing poly- (PEG) and oligo(ethylene glycols) (OEG), (-O-CH@sub 2@-CH@sub 2@-)@sub n@. For surface-grafted PEG, protein resistance is associated with an unfavorable change in the free energy when a protein approaches the surface and thereby compresses and dehydrates the polymer chains. However, this mechanism cannot explain the inertness of rigid, and thus conformationally restricted, OEG terminated alkanethiolate self-assembled monolayers (SAMs). Proposed models suggest the importance of water/SAM interactions at the surface or relate protein resistance to repulsive electrostatic forces. Due to its capability to characterize biological interfaces in situ, neutron reflectometry provides a unique tool to address fundamental questions of protein repulsion. We have studied the importance of interfacial water layers between inert SAMs and the bulk water phase to repel proteins. Temperature dependent studies on the OEG/water interface reveal, that a previously observed, density reduced water phase in the vicinity of the SAM cannot account for the protein resistant properties of the films. Moreover, neutron reflectometry has been used to investigate protein/surface interactions employing biomolecules in their native state and natural environment. Room temperature measurements on protein resistant films of OEG in contact with bovine serum albumin (BSA) solutions reveal the presence of an extended protein depletion layer between the SAM and the bulk protein solution. The results are compared to the strength and range of repulsive forces measured by AFM.

9:40am **BI-MoM5 Soft Interfaces on the Nanometer Scale - How Neutrons Contribute to a Deeper Understanding on the Supramolecular Level*, R. Steitz,*** Hahn-Meitner-Institut, Germany*; C. Czeslik,* Universität Dortmund, Germany*; H. Haas,* MediGene AG, Germany*; P. Riccio,* Università degli Studi della Basilicata, Italy **INVITED**

Current problems in soft matter and biomaterial science often require insight on the nanometer scale. In this contribution we will show how neutron reflectivity contributes to a deeper understanding of systems that are also of biological interest. Topics of increasing complexity and biological relevance will be discussed: Chapter one will focus on the properties of ultrathin polyelectrolyte coatings at a solid-liquid interface.@footnote 1@ Chapter two will show how these polymer coatings can be utilized as soft cushions for lipid membranes that form in situ by vesicle fusion from the liquid phase (under physiological conditions), or as switchable binding sites for proteins that penetrate from the aqueous solution.@footnote 2@ Number three will demonstrate the successful in situ assembly of myelin model membranes at a polymer-liquid interface, while number four will focus on the molecular organization within such membranes@footnote 3@ and their respective degradation upon reduced humidity. @FootnoteText@ @Footnote 1@ R. Steitz, V. Leiner, R. Siebrecht and R. v. Klitzing, Colloids and Surfaces A. 163, 63-70 (2000). @Footnote 2@ C. Czeslik, G. Jackler, R. Steitz and H.-H. von Grünberg, J. Phys. Chem. B 108, 13395 (2004). @Footnote 3@ H. Haas, M. Torielli, R. Steitz, P. Cavatorta, R. Sorbi, P. Riccio, A. Gliozzi, Thin Solid Films, 329, 627 (1998).

10:20am **BI-MoM7 Design & Structural Characterization of Amphiphilic 4-Helix Bundle Peptides Vectorially-Oriented at Soft Interfaces*, J.K. Blasie*,** *J. Strzalka, S. Ye, T. Xu, E. Nordgren,* University of Pennsylvania*; S. Satija,* National Institute of Standards and Technology*; I. Kuzmenko, T. Gog,* Argonne National Laboratory **INVITED**

Amphiphilic 4-helix bundle peptides have been designed to incorporate both biological and non-biological cofactors. An ensemble of these peptide-cofactor complexes, vectorially oriented at a soft interface between polar and non-polar media, can provide for the translation of their designed molecular function into a macroscopic material property of the interface. Such amphiphilic 4-helix bundle peptides can also serve as model integral membrane proteins for vectorial incorporation into a lipid bilayer providing a molecular laboratory for the detailed study of structure-function correlations. For example, the mechanism by which anesthetic binding to a designed cavity within its hydrophilic domain modulates the ion channel activity of its hydrophobic domain. Detailed structural studies of these amphiphilic peptides within such non-crystalline ensembles can be performed utilizing an essential combination of x-ray scattering, neutron scattering, and molecular dynamics simulation techniques.

11:00am **BI-MoM9 Structural Analysis of Phospholipid Membranes and Toxin Assault*, T.L. Kuhl*,** *C.E. Miller, T. Gog, K. Kjaer, J. Majewski,* University of California, Davis **INVITED**

In nature, membranes perform several functions of the living cell from selective transport and recognition, to simple sequestration. In general, the membrane consists of a single bilayer or in special cases, such as the lung surfactants, a single monolayer. Using powerful new neutron and x-ray sources, the techniques of reflectivity and grazing incidence diffraction permit us to obtain structural information on single lipid monolayers and supported bilayers in an aqueous environment. Recently, we demonstrated that 18 keV x-rays can be used to study lipid bilayers at the solid-liquid interface by x-ray reflectivity. We establish that this is a powerful technique for investigating biological systems in a previously inaccessible manner. Our measurements enabled the density distribution of single phospholipid bilayer membranes in bulk water to be measured with unprecedented precision enabling subtle variations in leaflet segregation to be resolved. Recent results on membrane perturbation by toxin binding will also be highlighted. In this case, scattering techniques enable us to distinguish binding and subsequent penetration of lipid layers upon toxin activation.

DNA Topical Conference
Room 311 - Session DN+BI-MoM

DNA Structures and Surfaces

Moderator: D.G. Castner, University of Washington

8:20am **DN+BI-MoM1 Design Rules for the Assembly of DNA Modified Nanoparticles: Influence of Surface Chemistry, Ionic Strength, and a Polycation*, K.J. Jeong*,** *S. Bhattacharya, D.B. Janes, G.U. Lee,* Purdue University

DNA-modified gold nanoparticles are promising materials for the efficient assembly of hierarchical nanostructures because of their ability to self-assemble specifically. In this study, the affect of the DNA surface immobilization chemistry, ionic strength of the solution, and a polycation on the efficiency of assembly of DNA-modified gold nanoparticles on DNA-modified gold surfaces was quantitatively studied. The hybridization efficiency was studied for DNA gold nanoparticles on DNA surfaces treating with 6-mercapto-1-hexanol (MCH) and it was found to significantly enhance the density of nanoparticles found on the surface. Ionic strength played a complex role on the observed assembly of the particles. In pure water, no assembly was possible because the diffusion of the nanoparticles was prevented by strong electrostatic repulsion. In ionic strengths greater than 0.1M NaCl, electrostatic repulsion was effective only at short ranges so that the nanoparticles can assemble through DNA hybridization. However, at ionic concentrations greater than 0.4M NaCl, a slight decrease in assembly was observed, which is attributed to the partial loss of particles in solution through aggregation. Theoretical analysis of these results based on the surface forces that govern the interactions between DNA-modified gold surfaces - electrostatic, van der Waals, and steric forces - confirms the interpretation above. One important conclusion drawn from the theoretical analysis is that the forces that govern the stability of DNA-gold colloids are not DLVO forces but a mixture of electrostatic and steric interactions. Spermidine, a polycation, was used to irreversibly lock-in the nanoparticles assembled on the surface so that the samples could be rinsed with water and dried. The results found in this article provide new insight into design rules for controlling the efficient assembly of DNA-modified nanoparticles.

8:40am **DN+BI-MoM2 DNA and Protein Microarray Printing on Silicon Nitride Waveguide Surfaces*, P. Wu,*** Colorado State University, US*; P. Hogrebe,* MSU*; D.W. Grainger,* Colorado State University

All bioanalytical assays using surface-capture of target analytes suffer from non-ideal sensitivity and selectivity. We have recently focused on microarray formats on optical waveguide surfaces to improve assay performance. Sputtered silicon nitride optical waveguide surfaces were silanized and modified with a hetero-bifunctional crosslinker to facilitate thiol-reactive immobilization of contact-printed DNA probe oligonucleotides, streptavidin and murine anti-human interleukin-1b capture agents in microarray formats. X-ray photoelectron spectroscopy (XPS) was used to characterize each reaction sequence on the native silicon oxynitride surface. Thiol-terminated DNA probe oligonucleotides exhibited substantially higher surface printing immobilization and target hybridization efficiencies than non-thiolated DNA probe oligonucleotides: strong fluorescence signals from target DNA hybridization supported successful DNA oligonucleotide probe microarray fabrication and specific capture bioactivity. Analogously printed arrays of thiolated streptavidin and non-thiolated streptavidin did not exhibit noticeable differences in either surface immobilization or analyte capture assay signals. Non-thiolated anti-human interleukin-1@beta@ printed on modified silicon nitride surfaces reactive to thiol chemistry exhibited comparable performance for capturing human interleukin-1@beta@ analyte to commercial amine-reactive microarraying polymer surfaces in sandwich immunoassays, indicating substantial non-specific antibody-surface capture responsible for analyte capture signal.

9:00am **DN+BI-MoM3 DNA: Not Merely the Secret of Life*, N.C. Seeman,*** New York University **INVITED**

Structural DNA nanotechnology uses the concept of reciprocal exchange between DNA double helices to produce branched DNA motifs, like Holliday junctions, or related structures, such as double crossover (DX), triple crossover (TX), paranemic crossover (PX) and DNA parallelogram motifs. We have worked since the early 1980's to combine DNA motifs, using sticky-ended cohesion, to produce specific structures. From branched junctions, we have constructed DNA stick-polyhedra, whose edges are double helices, and whose vertices are the branch points of DNA branched junctions. These include a cube, a truncated octahedron, and an irregular graph. We have also made topological targets, such as deliberately designed knots and Borromean rings. Recently, we have begun to template the topology of industrial polymers, such as nylon, with DNA-like scaffolds. Nanorobotics are key to the success of nanotechnology. We have used two DX molecules to construct a DNA nanomechanical device by linking them with a segment that can be switched between left-handed Z-DNA with right-handed B-DNA. PX DNA has been used to produce a robust sequence-dependent device that changes states by varied hybridization topology. The sequence-dependent nature of this device means that a variety of them attached to a motif can all be addressed individually. Recently, we have used this device to make a translational machine. A central goal of DNA nanotechnology is the self-assembly of periodic matter. We have constructed micron-sized 2-dimensional DNA arrays from DX, TX and two kinds of parallelogram motifs. We can produce specific designed patterns visible in the AFM from DX and TX molecules. We can change the patterns by changing the components, and by modification after assembly. In addition, we have generated 2D arrays from DNA parallelograms. These arrays contain cavities whose sizes can be tuned by design. Recently, we have used robust triangular motifs to produce honeycomb-shaped arrays.

9:40am **DN+BI-MoM5 Adsorption of DNA-wrapped Carbon Nanotubes on SAM Modified Gold Surfaces*, R.A. Zangmeister,*** *A.M. Opdahl, M.J. Tarlov,* NIST

We are studying the structure of DNA-wrapped carbon nanotubes (CNTs) on gold surfaces modified with alkanethiol self-assembled monolayers (SAMs). Our goal is to understand how DNA-wrapped CNTs interact with surfaces of varying chemical functionality and to use this knowledge to develop general strategies for controlling the assembly and alignment of DNA-wrapped CNTs on surfaces. Recently, Zheng and coworkers found that single-stranded DNA wraps around CNTs, improving their solubility in aqueous solutions and enabling their separation according to diameter and electronic properties.@footnote 1@ We postulate that the well-defined nature of the DNA-conjugated CNTs will allow their precise assembly and alignment on surfaces. We have examined the adsorption of DNA-wrapped CNTs on hydrophobic, hydrophilic, charged, and spatially patterned alkanethiol SAMs on gold. These samples are characterized using reflection absorption FTIR, scanning electron microscopy, and scanning probe microscopy. We have found that DNA-wrapped CNTs preferentially adsorb to positively charged amine terminated SAMs and to bare gold surfaces versus hydrophobic methyl terminated or negatively charged carboxylic acid terminated SAMs, indicating that electrostatic interactions play a major role in the deposition of these materials. In addition, general strategies for controlling the density and alignment of DNA-wrapped CNTs using alkanethiol SAMs will be discussed. @FootnoteText@ @footnote 1@Zheng, M., et al. Nature Materials 2003, 2, 338-342.

10:00am **DN+BI-MoM6 Surface Characterization of DNA Immobilization on Silane-modified SiO@sub x@*, G.M. Harbers,*** Colorado State University*; L.J. Gamble, D.G. Castner,* University of Washington*; D.W. Grainger,* Colorado State University

Fundamental studies must better understand and characterize DNA-immobilized surfaces to improve DNA microarray assay performance. DNA probe immobilization and target capture in microarray formats are quantified with standard fluorescence and radiometric assays. However, stable, efficient bulk immobilization methods that faithfully replicate microarray formats, but also permit high-sensitivity surface analysis with XPS and NEXAFS, are desired. While thiol-immobilized DNA probes on gold remain popular, silane coupling layers on oxides are more practical by closely duplicating commercial polymer microarray slides. Yet, silane coupling remains problematic, and common amine-terminated silane chemistry requires heterobifunctional crosslinking to immobilize thiol- or amine-modified oligo-DNA. Both commercial microarray substrates and silanated surfaces contain C, O, and N, confounding DNA surface analysis. Although phosphorus (at ~ 5%) is unique to DNA, at low DNA densities, P is difficult to detect and its XPS binding energies overlap with silicon plasmon peaks, making analysis confusing. Therefore, we compare silane coupling agents and substrates lacking nitrogen to follow unique DNA nitrogen and when possible phosphorus signals. Several amine- and thiol-reactive silanes on silicon oxide substrates were monitored with XPS at each surface coupling stage. In addition to a qualitative assessment of DNA density using XPS with expected N/P ratios of ~3.8, immobilized oligo-DNA densities and hybridization efficiencies were quantified using @super 32@P-DNA radiolabeling. DNA densities scaled with oligo-DNA feed concentrations (5nM-2µM) and target hybridization depended on oligo-DNA densities, ranging from ~100% at low densities (~10@super 11@ molecules/cm@super 2@) to <10% at high densities (~10@super 13@ molecules/cm@super 2@). NEXAFS, used to determine oligo-DNA probe and target duplex orientation, demonstrated little to no DNA surface orientation under these conditions.

10:20am **DN+BI-MoM7 From Fundamental Properties to Applications of DNA Monolayers*, R. Levicky,*** Columbia University **INVITED**

We investigate self-assembled DNA monolayers on metal and dielectric supports. Chains ranging in size from oligonucleotides to gene-sized polymers have been site-specifically attached without detectable side reactions in an end-tethered, "polymer brush" geometry. On metal supports, polythiol-mediated anchoring can be used to provide highly permanent immobilization of the nucleic acid. X-ray photoelectron spectroscopy (XPS), dynamic light scattering, and electrochemical methods have been applied to investigate the charging behavior, counterion partitioning, and organization of DNA monolayers on metal supports, and to evaluate label-free electrochemical approaches for monitoring interfacial hybridization reactions. The interfacial capacitance of end-tethered DNA films has been interpreted within a polyelectrolyte brush model. The observed trends with ionic strength and strand surface coverage generally agree with physical expectations, although as yet not understood increase in capacitance with decrease in ionic strength is observed for densest monolayers. Diagnostic applications are being pursued through development of near-field imaging methods and of active microelectronic substrates that integrate signal detection and processing functionality "on-chip." Near-field measurements offer a label-free technique with a sensitivity comparable to that of fluorescence-based systems currently in widespread use. Microelectronic biochips replace costly macroscopic instrumentation by integration of equivalent function within the solid support, using affordable CMOS microfabrication. Results from validation studies of these emerging technologies and their promise for more portable, simplified, and economical assays will be also described.

11:00am **DN+BI-MoM9 Electric Field Assisted Assembly of 2D and 3D DNA Nanostructures*, M.J. Heller,*** University of California, San Diego **INVITED**

Active microelectronic arrays which have been developed for genomic research and DNA diagnostic applications may also have potential for nanofabrication applications. These microarray devices are able to create reconfigurable electric field transport geometries on their surface which allows charged reagent and analyte molecules (DNA, RNA, oligonucleotide probes, amplicons antibodies, proteins, enzymes, nanoparticles and micron sized semiconductor devices) to be moved to or from any of the microscopic test sites on the device surface. These microelectronic array devices have the potential for many nanofabrication applications, including the directed self-assembly of molecular, nanoscale and microscale components into more complex 2D and 3D nanostructures and for creating higher-order mechanisms. This type of electric field assisted self-assembly using active microelectronic arrays is also being investigated as a method to carry out the selective functionalization of nanocomponents with high precision.

11:40am **DN+BI-MoM11 New Approach in Electrochemical DNA Hybridization Detection with Adjacent Impedance Probing**, ***K.S. Ma***, *H. Zhou, J. Zoval, M. Madou,* University of California, Irvine

Over the past two decades, the rapidly progressing development of electrochemical DNA biosensors have attracted substantial research efforts. Within the large number of electrochemical detection approaches, self-assembled monolayers (SAM) have been shown to be a convenient technique for immobilization of oligonucleotides probes on the gold electrodes. With this type of surface preparation, thiol-labeled ssDNA spontaneously adsorbs onto the gold surface, however, both via thiol-gold linkage (specific) and via non-specific interactions, thus introducing undesirable random orientations of the ssDNA molecules. These random orientations are undesirable because of the resulting non-perfectly-polarized membrane on the electrode. To avoid the problems caused by non-specific adsorption of probes on electrode surface, many methods have been studied intensively. Paleek et al. worked on a new assay method called the "two-surface strategy". In our current study, a unique method was employed for DNA hybridization detection. Using micro-fabrication processes, the two-surface concept was proved to be feasible in the same spatial domain. In this case, the DNA hybridization microspot is made for the bio-recognition event and a bare adjacent conductor electrode is designed for generating the impedance change through insulator deposition. The Electrochemical Impedance Spectroscopy was employed for the measurements. At medium frequency, a noticeable increase of impedance modulus appeared in the Bode plot. For non-complementary measurement, there was no change of impedance modulus. By this biosensor, upon DNA hybridization and subsequent deposition of the enzymatic reaction product, we had found significant improvement on the signal of DNA hybridization detection. Further studies such as lowest detection limitation are required before any practical applications.

Electronic Materials and Processing
Room 310 - Session EM+NS-MoM

Novel Approaches in Wide Bandgap Semiconductors

Moderator: C.R. Eddy Jr., U.S. Naval Research Laboratory

8:20am **EM+NS-MoM1 Halide Chemical Vapor Deposition of SiC Crystals**, ***M. Skowronski***, *A.Y. Polyakov, H.J. Chung, S. Nigam, S.W. Huh,* Carnegie Mellon University*; M.A. Fanton,* Pennsylvania State University **INVITED**

A novel approach to the high growth rate deposition of silicon carbide single crystals and layers is described. The Halide Chemical Vapor Deposition (HCVD) process uses tetrachlorosilane, propane, and hydrogen as reactants . The use of halogenated Si source and separate injection of Si and C precursors allows for preheating the source gases up to the growth temperature (2300 K) without causing premature chemical reactions. This is a distinct advantage over approaches employing silane as the Si precursor. The stoichiometry of HCVD crystals can be controlled by changing the C/Si flow ratio and can be kept constant throughout growth, in contrast to the Physical Vapor Transport technique. HCVD allows for growth of high crystalline quality, very high purity 4H- and 6H-SiC crystals with growth rates in 0.1-0.3 mm/hr. The densities of deep electron and hole traps are determined by growth temperature and C/Si ratio and can be as low as that found in standard CVD epitaxy. At high C/Si flow ratio, the resistivity of HCVD crystals exceeds 1E5 Ohm cm. The properties of crystals grown by HCVD make an attractive method for applications in high-frequency and/or high voltage devices.

9:00am **EM+NS-MoM3 Nm-Resolution Study of Various Quantum-Well Inclusions in 4H-SiC using Ballistic Electron Emission Microscopy: Quantum-Well Energy Depth and Local Transport Behavior**, ***K.-B. Park***, *J.P. Pelz,* The Ohio State University*; M. Skowronski, J. Grim, X. Zhang,* Carnegie Mellon University*; M.A. Capano,* Purdue University

Thin planar inclusions with local cubic stacking can form in hexagonal SiC during device operation, processing, or growth. These have been found to behave as electron quantum wells (QWs), and strongly impact material and device property. We have used nm-resolution Ballistic Electron Emission Microscopy (BEEM)@footnote 1@ to study the electronic properties of individual "single stacking-fault (1SF)" cubic inclusions forming during p-i-n diode operation in (1 1 -2 0) oriented 4H-SiC, where the inclusions intersect a Pt Schottky Barrier (SB) interface. BEEM indicates a QW energy depth of ~0.25 eV below the host 4H-SiC for these 1SF inclusions, comparable to a previous calculated energy of ~0.22 eV@footnote 2@ and a reported ~0.282 eV energy measured by luminescence quenching.@footnote 3@ We are also currently studying inclusions of a different structure forming during CVD growth on 8° miscut n-type 4H-SiC substrates. BEEM indicates a QW energy depth of ~0.40 eV for these inclusions, between the measured ~0.25 eV depth of 1SF inclusions and the ~0.53 eV depth we previously measured on "double" SF inclusions forming during high-temperature processing@footnote 1@. We also observe that the local BEEM current amplitude and SB height on the surrounding 4H-SiC material are quite different on either side of these inclusions, possibly due to strong spontaneous polarization in 4H-SiC and/or subsurface scattering from the 8° inclined inclusion. Work supported by ONR and NSF. @FootnoteText@ @footnote 1@ Y. Ding, K. -B. Park, J. P. Pelz, K. C. Palle, M. K. Mikhov, B. J. Skromme, H. Meidia, and S. Mahajan, Phys. Rev. B 69, 041305(R) (2004).@footnote 2@ H. Iwata et al., Mater. Sci. Forum 389-393, 533 (2002).@footnote 3@ S. G. Sridhara et al., Appl. Phys. Lett. 79, 3944 (2001).

9:20am **EM+NS-MoM4 Quantitative Assessment of Diffusivity and Specularity of Textured Surfaces for Light Extraction in Light-Emitting Diodes**, ***Y.A. Xi***, *X. Li, J.K. Kim, F. Mont, Th. Gessmann, H. Luo, E.F. Schubert,* The Future Chips Constellation

Light extraction in GaN-based light-emitting diodes (LEDs) is limited by the large difference of the refractive index between GaN and the ambient material. The texturing of surfaces and interfaces can improve the light-extraction efficiency into the surrounding medium. Surface-textured reflectors fabricated by natural lithography and ion-beam etching are shown to have a specular as well as a diffusive component of the reflectivity. The diffusely reflected power and the specularly reflected power of surface-textured reflectors are measured and analyzed quantitatively in terms of a new theoretical model. The diffusivity, that is diffusive-power-to-total-power ratio, is determined and shown to strongly depend on the surface texture. Diffusivities of 38.1% and 42.8 % are obtained for the reflectors masked with 445 nm and 740 nm nano-polystyrene balls, respectively, much higher than the 0.35 % of a planar Silver reflector. The light-extraction efficiency from a waveguide, clad by a partially diffuse reflector, is analyzed and shown to be enhanced. In addition, the spatial transmittance pattern of the textured surface is also measured and analyzed by using the same theoretical model. Our study shows that this model can be used to quantitatively assess the dependence of the light-extraction efficiency on the diffusivity of textured surfaces in GaN-based LEDs.

9:40am **EM+NS-MoM5 MOCVD Growth of Al-rich AlGaN Alloys: Materials for Deep-UV Emitters**, ***A.A. Allerman***, *M.H. Crawford, S.R. Lee, D.M. Follstaedt, P.P. Provencio, K.H.A. Bogart, A.J. Fischer,* Sandia National Laboratories **INVITED**

Solid-state light sources emitting at wavelengths less than 300nm would enable technological advances in many areas such as fluorescence-based biological agent detection, non-line-of-sight (NLOS) communications, water purification, and industrial processing. Emitters achieving such emission wavelengths have been fabricated using, almost exclusively, Al-rich alloys of AlGaN. However the growth of Al-rich AlGaN alloys, and especially AlN, has proven problematic owing to their extreme sensitivity to growth conditions in addition to the lack of a native substrate. Even though AlN substrates are being developed commercially, nearly all LEDs emitting in the deep UV are grown on sapphire substrates. Typical LED structures start with an AlN buffer layer which establishes much of the basic crystal structure for the device. The AlN layer typically exhibits threading-dislocation densities exceeding 1x10@super 10@cm@super -2@ and will experience stress-induced cracking when the layer exceeds approximately 1µm in thickness. In this presentation, we will describe a method for AlN film growth that produces threading-dislocation densities less than 5x10@super 9@cm@super -2@. This method involves manipulation of growth conditions following initial film nucleation and has been used to grow crack-free AlN films exceeding 3µm in thickness. Using these AlN films as template layers, we produced Si-doped AlGaN films (with ~50-70% AlN mole fractions) that have improved electron mobilities and higher doping efficiencies. These improvements suggest a reduced level of compensation in the AlGaN film due to reductions in dislocation density. The presentation will also include the performance of LEDs emitting in the deep UV (<300nm) that have been fabricated with lower dislocation density AlN-AlGaN films. Sandia is a multiprogram laboratory operated by Sandia Corporation, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-ACO4-94AL85000. This work is also supported by DARPA under the SUVOS program managed by LTC J. Carrano.

10:20am **EM+NS-MoM7 High Reflectance GaN-based Distributed Bragg Reflectors Grown on Si Substrates*, M.A. Mastro*,** *R.T. Holm, N.D. Bassim, D.K. Gaskill, C.R. Eddy Jr., R.L. Henry, M.E. Twigg,* U.S. Naval Research Laboratory

Presently, GaN based optoelectronic devices are primarily grown on expensive sapphire and SiC substrates. Substituting these substrates with inexpensive Si substrates would represent a major shift in the economics of the visible optoelectronic market. The primary limitation to this device structure is light absorption by the opaque Si substrate. Insertion of a high reflectance distributed Bragg reflector (DBR) between the substrate and the active region would increase light extraction by approximately a factor of two. The second major impediment to this device structure is the poor quality of group III-nitride films grown on Si substrates. High densities of dislocations and cracks can form in the (Al,Ga,In)N layers due to their large lattice and thermal expansion mismatch with the Si substrate. Thus low internal quantum efficiency is commonly observed for GaN based devices grown on Si substrates. This paper presents the first high-reflectance (>90%) (Al,Ga)N quarter-wave DBR grown on a Si (111) substrate. In-situ reflectometry of the MOCVD growth process allowed exact control of each individual layer thickness to yield DBR reflectance approaching the calculated theoretical level. Nominally crack free structures were obtained by controlling the distribution of the strain in the structure. Specifically, the DBR structure acted as a distributed buffer layer (DBL) for the thick GaN cap layer. TEM revealed a fall-off in screw-type dislocations throughout the DBL. This development presents the opportunity to significantly advance GaN based optoelectronics, including light emitting diodes (LEDs), resonant cavity light emitting diodes (RCLEDs) and vertical cavity surface emitting lasers (VCSELs), on Si substrates.

10:40am **EM+NS-MoM8 Synthesis of Aligned Arrays of III-Nitride Nanowires and Heterostructure Nanowires via MOCVD*, G.T. Wang*,** *J.R. Creighton, P.P. Provencio,* Sandia National Laboratories*; D. Werder,* Los Alamos National Laboratory

Nanowires based on the direct bandgap semiconductor Group III nitride (AlGaInN) materials system are attractive due to their potential in novel optoelectronic applications, including LEDs, lasers, high power transistors, and sensors. We have employed a MOCVD process to synthesize highly aligned arrays of single-crystalline GaN nanowires in a standard cold-wall rotating disk reactor on 2-inch diameter sapphire wafer substrates without patterning or the use of a template. Building on this process, we have also been able to synthesize novel core-shell heterostructure nanowires consisting of a GaN cores and various III-nitride shell materials, including AlN, InN, and AlGaN, and InGaN. In this presentation, several challenges and issues regarding control of the growth process will be discussed, including selectivity of VLS growth versus film nucleation, control of nanowire alignment and density, as well as the ability to control shell-layer uniformity in heterostructure nanowires will be discussed. Data on the optoelectronic and electrical properties of the nanowires and heterostructure nanowires will also be presented. The growth processes and reactor environment employed in this study are typical of those used to synthesize device-quality III-nitride films and should be scalable to larger commercial reactors and substrates. 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 **EM+NS-MoM9 Large-scale Synthesis of GaN Nanowires by Direct Reaction of Gallium with Ammonia*, C.-H. Hsieh,*** National Tsing Hua University, Taiwan, R.O.C.*; L.-J. Chou,* National Tsing Hua University, Taiwan, R.O.C., Taiwan, R.O. C.

High-density GaN nanowires were synthesized on a large-scale Si substrate by direct reaction of metal gallium vapor under ammonia and hydrogen gases at 680~700°C. The morphology, composition and crystal structure were characterized by field-emission scanning electron microscope (FESEM, JSM-6500F), field-emission transmission electron microscope (FETEM, JEM-3000F) and X-ray spectrometer (SHINMADZU), respectively. From SEM images, the morphology of GaN nanowires is vermicular-like with average diameter of 200 nanometer and the length of up to 20 micrometer. The compositional line profile of TEM analysis revealed the vermicular-like GaN nanowires were uniformly doped with silicon and oxygen. The correspondent electron diffraction pattern indicated the vermicular-like GaN nanowires exhibiting poly-crystal structure. The XRD results of vermicular-like GaN nanowires show the hexagonal wurtzite structure. Furthermore, the cathodoluminescence (CL) characteristics demonstrate a broad band in the energy range of 2.1-3.1eV.

11:20am **EM+NS-MoM10 Optical and Ellipsometric Studies on InN Layers Grown by High-Pressure CVD*, N. Dietz*,** *M. Alevli, M. Strassburg, V.T. Woods, U. Perera,* Georgia State University*; N.A. Stoute,* North Carolina State University, US*; D.E. Aspnes,* North Carolina State University

The fabrication of emerging detector and emitter structures as well as high-frequency/high-power devices operating at high temperature(s) that are based on group III-nitride compound alloys is presently limited by the challenging difficulties in the growth of high quality In-rich group-III-nitride alloys and heterostructures. Even though recent improvements in MBE-grown InN material established a band gap near 0.65 eV, other data show a band gap near 1.85 eV. The origin of this bandgap difference is not understood. Here, we focus on the analysis of optical data obtained both by absorption spectroscopy and spectroscopic ellipsometry (SE) on InN material grown by high-pressure chemical vapor deposition (HPCVD) in the 10 to 15 bar pressure range as a function of growth temperature, flow rate, and flow ratios of ammonia and trimethylindium (TMI). With HPCVD we can compensate the inherent volatility of nitrogen and stabilize indium-rich conditions and grow group-III-nitride alloys at temperatures comparable to those used for GaN and AlN. The optical data indicate that the decrease in optical absorption edge from 1.85 eV to 0.63 eV is caused by a series of absorption centers appearing at 1.6 eV, 1.35 eV, 1 eV, 0.87 eV and below 0.65 eV. The appearance of these centers correlates with the indium-to-nitrogen ratio, which is controlled through the flow rates of ammonia and TMI. For InN layers grown near 1100 K and molar ammonia/TMI ratios less than 200, an InN absorption edge below 0.63 eV is observed. For material with absorption edges near 1.9 eV a strong peak is observed, which appears to be excitonic in nature.

11:40am **EM+NS-MoM11 Determining Composition of HPCVD Indium Nitride with Auger Electron Spectroscopy*, R.P. Bhatta,*** *B.D. Thoms, V.T. Woods, M. Alevli, N. Dietz,* Georgia State University

Indium Nitride (InN), a wurtzite structure III-V semiconductor with a direct bandgap, has potential for use in many optoelectronic applications. In addition, alloys of InN, GaN, and AlN cover a large spectral range from 0.6 eV up to 6 eV which can be utilized in many novel optoelectronic devices. The low growth temperatures usually needed for growth and stability of InN have limited the use of widely varying alloy compositions in the same device. High pressure chemical vapor deposition (HPCVD) allows InN to be grown at temperatures similar to those of GaN and AlN. There has recently been considerable debate regarding the value of the energy bandgap of InN and its relationship to the concentration of oxygen in the film. The optical analysis of InN layers grown under HPCVD shows that the shift of the absorption edge down to 0.63 eV is caused by a series of absorption centers. The appearance of these absorption centers is closely related to the indium and nitrogen point defect chemistry, which can be controlled through the molar flow ratio of the precursors. In this contribution, the compositional analysis of HPCVD grown InN films by Auger Electron Spectroscopy (AES) is presented. The proximity of the nitrogen and indium AES peaks makes determination of nitrogen to indium ratios more difficult. It has been reported that ion sputtering reduces the nitrogen content in InN films. While this study also reports that sputtering reduces the relative peak-to-peak height for dN/dE spectra, a substantial reduction is not observed in the relative integrated intensities for undifferentiated spectra. We conclude that sputtering has a large effect on the lineshape of nitrogen AES peaks but does not substantially reduce the nitrogen concentration. The concentrations of contaminants such as carbon and oxygen were analyzed and correlated with film properties measured by Raman and absorption spectroscopy.

Electronic Materials and Processing
Room 309 - Session EM-MoM

Electronic Properties of High-k Dielectrics and their Interfaces

Moderator: S.A. Chambers, Pacific Northwest National Laboratory and Univ. of Washington

8:20am **EM-MoM1 Electronic Properties of High-K Dielectrics and their Interfaces*, J. Robertson,*** University of Cambridge, UK **INVITED**

The continued scaling of CMOS devices means that SiO2 must be replaced as gate oxide by a dielectric of higher dielectric constant (K) to minimise gate leakage.@footnote 1@. The presently preferred candidates are HfO2, its silicates and nitrided alloys. La oxide and LaAlO3 are possible in the future. The reasons for this selection in terms of band offsets will be given,@footnote 2@ including their measurement and calculation. Despite much success in developing growth methods for high K oxides, including ALD, presently the performance of FETs with HfO2 are worse than those with SiO2 in terms of threshold voltage shifts, carrier mobility and trapped charge. This arises partly from the more complicated interface structure and greater bonding possibilities than at an Si:SiO2 interface. We show it is possible to define an ideal abrupt Si:HfO2 interface in terms of its bonding; only Hf-O and Si-O bonds or only Hf-Si bonds.@footnote 3@ In fact, a number of high symmetry and lower symmetry abrupt interfaces are possible. The structure, electronic structure and band offsets for these are given. It is then possible to define a defective interface; one containing mixed bonding. It is shown how such mixed bonding at the "back interface" between the HfO2 and poly-Si gate may be the cause of the excessive gate threshold voltages.@footnote 4@@FootnoteText@@footnote 1@ J Robertson, "High dielectric constant oxides", Euro Phys J Appl Phys 28 265 (2004) @footnote 2@ J Robertson, "Band offsets of wide band gap oxides and implications for future electronic devices", J Vac Sci Technol B 18 1785 (2000) @footnote 3@ P W Peacock, J Robertson, "Bonding, energetics and band offsets of Si-ZrO2 high-dielectric constant gate oxide interfaces", Phys Rev Letts 92 057601 (2004) @footnote 4@ K Xiong, P W Peacock, J Robertson, "Fermi level pinning and Hf-Si bonds at HfO2: poly-Si gate electrode interfaces", App Phys Lett 86 012904 (2005).

9:00am **EM-MoM3 The Effect of Nitrogen Incorporation on the Material and Electrical Properties of HfO@sub 2@ on Si*, M. Sawkar,*** *J. Choi, R. Puthenkovilakam, J.P. Chang,* UCLA

Alternative gate dielectrics are required in the future generation of MOSFET devices to enable their rapid down-scaling. One of the most promising candidates is HfO@sub 2@. Unfortunately, HfO@sub 2@ has a low crystallization temperature, resulting in its structural change from amorphous to polycrystalline under high-temperature processing, which results in grain boundaries that serve as a path for leakage current, oxygen diffusion, and impurity diffusion. The incorporation of nitrogen in HfO@sub 2@ films increases the temperature at which the grain boundaries form allowing these films to remain amorphous at higher temperatures. This paper discusses the effect of nitrogen incorporation on the material and electrical properties of HfO@sub 2@. XPS, ellipsometry, and HRTEM are used to characterize the material properties. To characterize the electrical properties, MOS capacitors are fabricated to examine the capacitance-voltage (C-V) and current density-voltage (J-V) characteristics. Preliminary results showed that the leakage current density of the nitrogen incorporated samples is approximately three orders of magnitude lower than the as-deposited HfO@sub 2@. We also performed first-principle simulations within the framework of density functional theory to assess the effect of nitrogen incorporation on the bulk electronic properties of HfO@sub x@N@sub y@, as well as on the dielectric/Si interface properties. The simulation shows that the N 2p state is extended further toward the conduction band and the ionic character of Hf-N bonding is less pronounced with increasing nitrogen incorporation, resulting in a reduction in the band gap. The band alignment at the HfO@sub x@N@sub y@/Si interface calculated using the (HfO@sub 2@)(Hf@sub 3@N@sub 4@) structure as a model stoichiometry revealed an estimated valence-band offset of 1.14 eV, which is significantly lower than that reported for HfO@sub 2@/Si.

9:20am **EM-MoM4 Suppression of Fixed Charge at Internal Interfaces between SiO@sub 2@ and Dual-Layer High-k Gate Dielectrics: HfO@sub 2@-Al@sub 2@O@sub 3@*, C.L. Hinkle,*** *G. Lucovsky,* North Carolina State University

A reduction in interfacial fixed charge between SiO@sub 2@ and high-k dielectrics has been studied using a dual layer high-k stack to match intrinsic bonding properties at interfaces. Previous studies of Al@sub 2@O@sub 3@ on SiO@sub 2@ have shown a large amount of fixed charge at the interface, effectively eliminating Al@sub 2@O@sub 3@ from the discussion of alternative gate dielectrics. However, a self-organization occurs for Zr and Hf oxides and silicates after anneal that leaves low interfacial charge at the interface of those materials and an SiO@sub 2@ buffer layer. The density of interfacial defects has been shown to scale with the step in bonds per atom at the interface, D@sub int@ @alpha@ [N@sub av@(A) - N@sub av@(B)]@super 2@. Using this scaling as a guide, internal interfaces can be engineered from materials that match the average bonds per atom on both sides of the interface thereby reducing the number of defects and suppressing the fixed charge. A gate stack using SiO@sub 2@-HfO@sub 2@-Al@sub 2@O@sub 3@ has been produced using these techniques. The SiO@sub 2@-HfO@sub 2@ interface becomes self-organized and relatively defect low after anneal at 800°C whereas the HfO@sub 2@-Al@sub 2@O@sub 3@ interface has a matchup of N@sub av@ intrinsically. Electrical characterization of the gate stacks was done using C-V measurements to analyze the flatband voltage shift in these materials. The flatband voltage for the SiO@sub 2@-HfO@sub 2@-Al@sub 2@O@sub 3@ stack is effectively the same as a film of SiO@sub 2@ showing the reduction in fixed charge expected from the theory mentioned above. Different thicknesses of each layer have been studied as well as frequency dependent C-V to determine trapping at the internal interfaces. Using this proposed method extends the range of usable high-k materials.

9:40am **EM-MoM5 Self-organization of Thin Film Dielectrics and Their Interfaces in Gate Stacks for Advanced Si Devices*, G. Lucovsky,*** NC State University*; J.C. Phillips,* Rutgers University

Self-organizations which inhibit percolation of network bond-strain are addressed. These occur i) within multi-atom gate dielectrics, Si@sub 3@N@sub 4@:H and Si@sub 3@N@sub 4@-SiO@sub 2@-ZrO@sub 2@ alloys, ii) at Si-SiO@sub 2@ interfaces, and iii) at internal interfaces in multi-layer dielectrics. All are driven by the same mechanism, but the dimensionalities of the materials systems are different. The dielectric films are 3-dimensional, but interfaces are 2-dimensional. The self-organizations of Si@sub 3@N@sub 4@:H and Si@sub 3@N@sub 4@-SiO@sub 2@-ZrO@sub 2@ dielectrics arise from stressed-rigid bonding, and prevent percolation of bond-strain at processing temperatures greater than the deposition temperatures. For the Si@sub 3@N@sub 4@:H and Si@sub 3@N@sub 4@-SiO@sub 2@-ZrO@sub 2@ alloys, compositions are identified that prevent chemical phase separation, and subsequent degradation of device properties. At the Si-SiO@sub 2@ interface the self-organization is at a molecular scale in a layer ~0.3-0.5 nm thick. This self-organization relieves in-plane strain, and provides for the first time a quantitative understanding for roughness scattering of channel electrons/holes in field effect transistors. This self-organization has enabled the information science revolution to proceed by down-sizing of Si integrated circuits and making Moore's Law for performance, cost and increased functionality a reality. Finally, self-organization at SiO@sub 2@-high-k internal interface is enabling for continuing Moore's Law scaling with alternative high-k dielectrics such as HfO@sub 2@ and Al@sub 2@O@sub 3@.

10:00am **EM-MoM6 Physical and Electrical Properties of LaAlO@sub 3@, Potential Candidate for High K Gate Dielectric**, *V. Edon,* ***M.C. Hugon****, O. Voldoire, B. Agius,* Universite Paris Sud, France*; I.J.R. Baumvol, L. Miotti, K.P. Bastos,* Universidade Federal do Rio Grande do Sul, Brazil

There is currently an extensive research effort to find an alternative gate dielectric to replace SiO@sub 2@ in metal oxide semiconductor field effect transistors (MOSFETs). LaAlO @sub 3@ is a promising material: it has a dielectric constant in the range 20-27. RuO@sub 2@ is proposed as a gate electrode. LaAlO@sub 3@ films were deposited by rf magnetron sputtering of a LaAlO@sub 3@ target in argon atmosphere. Thin film properties are studied as a function of deposition parameters (rf power, process pressure) and thermal annealings (in @super 16@O@sub 2@ or @super 18@O@sub 2@ atmospheres - temperatures from 450 to 1000 °C). Physical properties of as deposited material (composition, density), as determined by RBS, NRA, and X-ray reflectometry, are seen to depend slightly on deposition parameters. The films are stoichiometric and present a density of 5.5 ± 0.5g.cm@super -3@ close to the bulk material one (6.5g.cm@super -3@). The thermal stability of LaAlO@sub 3@ has been investigated under typical conditions of a MOSFET processing. O and Al transport during annealings are investigated with sub-nanometric depth resolution via the narrow resonances of @super 18@O(p,@alpha@)@super 15@N at 151 keV (fwhm=100eV) and @super 27@Al(p,@gamma@)@super 28@Si at 404.9keV (fwhm=40eV) respectively. The interfacial characteristics of

LaAlO@sub 3@/Si were measured by spectroscopic ellipsometry, X ray reflectometry. The initial measurements subject the presence of an interfacial layer. We have performed high frequency (1MHz, 100kHz) C-V and I-V characteristics on RuO@sub 2@/LaAlO@sub 3@/Si MIS structure. After a thermal treatment at 600°C, the C-V curves exhibit well defined accumulation, depletion and inversion regimes which indicate a low interface state density. With the device biased in accumulation regime, a permittivity of 15 was deduced. Low leakage current is detected for films deposited at 0.5Pa or 5Pa and annealed at 600°C under 1 atm of oxygen.

10:20am **EM-MoM7 Magnesium Oxide as a High-K Gate Dielectric***, **L. Yan**, C.M. Lopez, E.A. Irene,* University of North Carolina-Chapel Hill

The presently considered candidate high @Kappa@ dielectric materials are reactive with Si and SiO@sub 2@ and most metals yielding undesirable interfacial electronic properties. While magnesium oxide (MgO) does not have as high of a @Kappa@ value (about 9.8 for bulk material) as many of the other candidate dielectrics (e.g., ZrO@sub 2@ and HfO@sub 2@), it has its unique advantages such as chemical inertness enabling sharp interfaces and wide bandgap (7.3 eV) for large band offsets with silicon (Si) to minimize leakage. In this study, MgO thin films were deposited via reactive rf sputtering on both bare Si and SiO@sub 2@ coated Si. In situ spectroscopic ellipsometry (SE) and Mass Spectrometry of Recoiled Ions (MSRI) were used to monitor the film growth in real time and cross-sectional transmission electron microscopy and atomic force microscopy were used to determine interface and surface roughness, respectively. Capacitance versus voltage (C-V) and conductance (G(@omega@)) versus gate voltage (G(@omega@)-V) measurements were performed on capacitor structures in order to determine @Kappa@, and the density of interface states (D@sub it@), respectively. Thus far a value of about 8 was obtained for the static dielectric constant for 10 nm films and interface charge and D@sub it@ results are comparable with SiO@sub 2@ on Si. Based on our measured properties it is concluded that thin MgO films can provide a high K dielectric for many electronic applications. @FootnoteText@ This work is supported by the National Science Foundation (NSF) Materials Research Division.

10:40am **EM-MoM8 Spectroscopic Studies of Band Alignment in Metal/High-k Dielectric/Si Gate Stacks***, **E. Bersch**, S. Rangan, O. Celik, W. Jiang, C.L. Hsueh, E. Garfunkel, R.A. Bartynski,* Rutgers University

The continued scaling of CMOS devices requires the replacement of SiO2 with a higher dielectric constant oxide, and of the doped poly-silicon gates with metal electrodes. The band alignment at these interfaces is critical in that there must be sufficient valence and conduction band offsets (> 1.0eV) to limit the leakage current across the dielectric to a tolerable level. We have measured the conduction and valence band offsets of metal/high-k/Si gate stacks with inverse photoemission and photoemission, respectively, for various combinations of candidate gate metals and alternate dielectrics, in situ. Using inverse photoemission, the conduction band minimum (ECBM) is found to be 2.2 eV above the Fermi level ALD grown HfO2/Si films. This value is reduced by ~ 0.3 eV on films annealed to 700oC. The energy of the CBM of hafnium silicate films grown on Si that were subjected to a 1000oC anneal is found to be independent of silicate concentration, while similarly processed nitrided hafnium silicate films annealed exhibit in increase in the CBM energy with increasing silicate concentration. Upon metallization with Ru, ECBM of each of these systems decreases by ~ 0.3eV. We have also measured these offsets on the same samples with x-ray absorption spectroscopy and internal photoemission. The results of all of these methods will be compared to each other, and the merits of each method will be discussed.

11:00am **EM-MoM9 Characterization of Nitrided Hafnium Silicates for High-@kappa@ Dielectrics Using Photoelectron Spectroscopy***, **A. Mathew**, K. Demirkan,* University of Delaware*; C.-G. Wang, G. Wilk,* ASM America*; R.L. Opila,* University of Delaware

Nitrided hafnium silicates are strong contenders to replace the silicon dioxide gate dielectric in transistors for low standby power applications. Photoelectron spectroscopy with its sensitivity to local chemical bonding is an invaluable tool for investigating this dielectric. Hafnium silicates were deposited using Atomic Layer Chemical Vapor Deposition and subsequently nitrided. Nitrogen incorporation prevents dopant diffusion from the poly-silicon. Rapid thermal annealing of the nitrided and as deposited films can induce spinodal decomposition of these films. The Hf 4f and Si 2p binding energies in unannealed, non-nitrided films change as a function of Hf/Si composition. This shift in binding energy is attributed to the electronegativity of second nearest neighbors. After annealing, the Hf 4f and Si 2p peaks do not vary as a function of composition, but are not at the silica 2p and hafnia 4f positions. The distribution of nitrogen in the film can be determined from photoelectron spectra collected as a function of take off angles. Results suggest that nitrogen replaces oxygen. The variation in the Hf 4f, Si 2p and N 1s binding energies as a function of annealing temperature and phase composition will be discussed. The effect of nitrogen upon the binding energies of the Hf 4f, O 1s and Si 2p before and after annealing, as well as its role in the phase decomposition upon annealing will be discussed.

11:20am **EM-MoM10 Surface Functionalization and Interface Characterization for HfO@sub 2@ Growth by Atomic Layer Deposition***, **Y. Wang**, M.-T. Ho, L.S. Wielunski, L.V. Goncharova, T. Gustafsson, Y.J. Chabal,* Rutgers University*; N. Moumen,* Sematech*; M.P. Boleslawski,* Aldrich Chemical Co.

Hafnium oxide is a promising candidate to replace SiO@sub 2@ and prevent current leakage in nanoscale transistors. For fabricating ultra-thin films, atomic layer deposition (ALD) is the preferred growth method. However, formation of interfacial SiO@sub 2@ during the ALD growth significantly increases the equivalent oxide thickness (EOT), partly negating the value of high-@kappa@ dielectrics. Our approach to minimizing interfacial SiO@sub 2@ formation during HfO@sub 2@ deposition is based on surface pretreatment of H-passivated silicon surfaces with Cl@sub 2@ and NH@sub 3@, followed by studies of the effect of post annealing on the nature of the interface. Using various surface/interface analytical techniques, such as in situ infrared spectroscopy, ex situ Rutherford back scattering spectroscopy (RBS) and medium energy ion scattering spectroscopy (MEIS), we have found that surface termination/passivation by hydrogen, chlorine, or silicon nitride can effectively prevent silicon oxidation during HfO@sub 2@ ALD growth, while fostering a linear growth of HfO@sub 2@ (~0.09 nm per ALD cycle). In situ IR studies show a linear incorporation of hydroxyl within the HfO@sub 2@ film during growth, constituting a source of excess oxygen within the film. Upon annealing above 400@super o@C, interfacial SiO@sub 2@ is formed as the hydroxyl content of the film decreases down to less than 10% of the initial value. The initially amorphous HfO@sub 2@ film begins to crystallize at 500@super o@C, as reflected in the appearance of a sharper HfO@sub 2@ phonon mode (~780 cm@super -1@) and in the angular dependence in the MEIS. Preliminary electrical properties measurement indicates the leakage current of the ALD-grown HfO@sub 2@ is small on the pre-functionalized silicon substrate.

11:40am **EM-MoM11 Differences in Band Edge Electronic Structure between Nanocrystalline ZrO@sub 2@ and HfO@sub 2@ Thin Films, and Bulk Crystals and Thin Films of Cubic Zironia (ZrO@sub 2@-Y@sub 2@O@sub 3@) and Hafnia (HfO@sub 2@-Y@sub 2@O@sub 3@)***, **N.A. Stoute**,* North Carolina State University, US*; H. Seo, C.C. Fulton, D.E. Aspnes, G. Lucovsky,* North Carolina State University

There is considerable interest in the band edge electronic structure of high-k oxides for applications as gate dielectrics in advanced semiconductor devices. This paper compares band edge electronic structure of nanocrystalline (nc) thin films of ZrO@sub 2@ and HfO@sub 2@, with i) bulk crystals of cubic zirconia and hafnia, e.g., ZrO@sub 2@ that is cubic as a result of incorporation of 5%-30% Y@sub 2@O@sub 3@, as well as ii) thin alloys of nanocrystalline ZrO@sub 2@-Y@sub 2@O@sub 3@ over a wider composition range. The band edge electronic structure of these alloy dielectrics has been studied by visible-near UV optical transmission and visible-near-UV-VUV spectroscopic ellipsometry. Band edge structure is also compared with ab initio calculations. For (Y@sub 2@O@sub 3@)@sub 0.095@(ZrO@sub 2@)@sub 0.905@ we observe a sub-bandgap absorption onset at ~4 eV, an absorption edge at ~5.3 eV and a weak d-state structure at ~6.3 eV. In contrast, nc-ZrO@sub 2@ has an absorption edge at ~5.7eV, and prominent d-state features at ~6.2 and 7.0 eV. Cubic (Y@sub 2@O@sub 3@)@sub 0.15@(HfO@sub 2@)@sub 0.85@ displays sub-bandgap absorption at ~ 4 eV, an absorption edge at ~5.9 eV, and a weak, broad d-state feature at ~7.5 eV, compared with an absorption edge at ~5.8 eV and sharp d-state features at ~6 and 7.2 eV in nc-HfO@sub 2@. The end-member ZrO@sub 2@ and HfO@sub 2@ nanocrystalline thin films display Jahn-Teller distortions that remove band edge d-state degeneracies that are not present in the Y@sub 2@O@sub 3@-stabilized cubic phases. The Y@sub 2@O@sub 3@-stabilized cubic phases display sub-bandgap absorption attributed to deep electronic states associated with the O-vacancies, while the nc-thin films display defects ~0.5 to 0.8 eV below the conduction band edge. These have been assigned to nanocrystalline grain boundary defects.

MEMS and NEMS
Room 207 - Session MN-MoM
Processing & Characterization of Materials for MEMS & NEMS

Moderator: S. Burkett, University of Arkansas

8:20am **MN-MoM1 Mechanical Properties of Polysilicon Thin Films using Micromachined Membranes and a Design of Experiments Methodology***, A.J. Fleischman, A. Dubnisheva, R.S. Butler,* The Cleveland Clinic Foundation*; R. Rosenblum,* ***C.A. Zorman,*** Case Western Reserve University*; S. Roy,* The Cleveland Clinic Foundation

The Youngs modulus, residual stress, and burst pressure of 4 micron-thick polysilicon films were determined from the load-deflection characteristics of suspended membranes. Specimens were prepared by the deposition of undoped amorphous Si films onto Si3N4 coated, Si wafers by LPCVD. The wafers (called Poly2) were annealed at 1100C for 1 hour to crystallize the films and lower the residual stress. For roughly 50% of the samples (called Poly1), a second identical annealing step was performed to evaluate changes in mechanical properties when such films are used in multilayer devices. Membranes that were 1.2 x 1.2 mm2 in area were fabricated by KOH-based anisotropic etching, using the underlying nitride film as an etch stop. Each test chip was subjected to pressure cycling tests using an interferometric load-deflection setup developed specifically for membrane evaluation. Data were collected using two test chip mounting schemes: (1) epoxy mounting, and (2) mechanical slot screw clamping. We found that mechanical clamping was sufficient to achieve the desired results with the added benefit that the specimens could be demounted without damage. A design-of-experiments testing methodology and one way ANOVA analysis at the 95% confidence interval was employed to factor out environmental and testing setup variables associated with the measurement technique. We found the Poly1 samples had an average Youngs modulus of 163 GPa and a residual stress of 121 MPa, while those for Poly 2 were 141 GPa and 23 MPa. The membranes were also evaluated for burst pressure in a setup capable of pressurizing the membranes well above the lowest average burst pressure of 78 psi. SEM analysis was used to examine the membranes after bursting. We found that the membranes did not delaminate, but rather failed at sites near the membrane edges. The presentation will detail the testing and data analysis procedures, as well as the use of these data in designing MEMS structures subject to failure.

8:40am **MN-MoM2 Characterization of Nanoscale Wear Processes in Polysilicon-Based MEMS Devices using AFM and PEEM-NEXAFS Spectromicroscopy***,* ***A.V. Sumant****, D.S. Grierson, G. Wabiszewski, R.W. Carpick,* University of Wisconsin at Madison*; A. Corwin, M. De Boer,* Sandia National Laboratories

We present studies aimed at elucidating mechanisms of nanoscale wear in polysilicon-based microelectromechanical systems (MEMS) devices. Current silicon-based MEMS devices that involve frictional sliding fail due to wear. Coating MEMS parts with self-assembled monolayers (SAMs), which act as lubricating and passivating layers, can improve the performance of these devices to some extent. However, devices coated with SAMs have finite lifetimes and can fail after unsuitably short periods of time. We seek to determine the precise causes of failure to ultimately improve the performance of MEMS devices. We use a atomic force microscopy (AFM) and PEEM-NEXAFS (Photoelectron Emission Microscopy combined with Near-Edge X-ray Absorption Fine Structure) spectromicroscopy to obtain quantitative information on structural damage and chemical changes inside the wear track of a MEMS device specifically designed to conduct friction and wear tests under controlled conditions. The ability of the PEEM-NEXAFS technique to spatially resolve and chemically characterize regions of interest is unparalleled and therefore ideally suited for this work. The results show for the first time that it is possible to detect chemical changes occurring within the micro-scale wear track. Furthermore, we are able to correlate the spectroscopically-observed features from the PEEM-NEXAFS measurements with AFM measurements of the modified surface topography in the wear track. One critical challenge is to minimize radiation damage of the SAMs due to synchrotron X-rays exposure during characterization. We show that by using radiation-blocking shutters and adjusting photon exposure and flux, damage can be reduced and reliable data can be obtained.

9:00am **MN-MoM3 Science and Technology of Ultrananocrystalline Diamond Thin Films and Their Integration for Fabrication of Advanced MEMS/NEMS***,* ***O. Auciello,*** Argonne National Lab*; J. Birrell,* Presently with Advanced Diamond Technologies*; J.A. Carlisle,* Argonne National Lab*; K.-H. Kim, B. Peng, H.D. Espinosa,* Northwestern Univ.*; A.V. Sumant, D.S. Grierson, N. Guoqing, R.W. Carpick,* Univ. of Wisconsin-Madison **INVITED**

The science and technology of multifunctional thin films and interfaces and new phenomena sustained in film-based nanostructures are opening the way for a new generation of multifunctional microelectromechanical and nanoelectromechanical system (MEMS/NEMS) devices. In this talk, we will review the fundamental and applied science related to the synthesis and characterization of ultrananocrystalline diamond (UNCD) thin films and their integration with other materials for the fabrication of advanced MEMS/NEMS devices. UNCD films are grown using a novel Ar-rich CH@sub 4@/Ar plasma chemistry that results in the synthesis of films with 3-5 nm grains and atomically abrupt grain boundaries, and it is this unique nanostructure that is responsible for the unusual combination of mechanical, tribological, chemical and electronic (when doped) properties of UNCD relevant to MEMS/NEMS. We will discuss results from joint research between Argonne and Northwestern University that provided unique insights into the mechanical properties of UNCD relevant to MEMS and NEMS as well as the fabrication of MEMS structures and characterization of their mechanical properties, We will also discuss results from joint research between Argonne and University of Wisconsin-Madison that provided unique insights into the effect of seeding layers such as W on the growth of UNCD films and on their morphology and microstructure and the resulting effects on nanoscale tribological and electrochemical properties, We will discuss characterization of the surface chemistry and bonding probed by total electron- and fluorescence-yield near edge x-ray absorption fine structure (NEXAFS) spectroscopy to distinguish between near-surface and deeper (“bulk”) changes in the film and correlations with tribological and electrochemical properties that depend sensitively on the surface chemistry and bonding. The fundamental and applied science of UNCD films will be discussed in view of fabrication of structures for advanced MEMS/NEMS devices. *Work supported by the U.S. Department of Energy, Basic Energy Sciences-Materials Sciences, under Contract W-31-109-ENG-38.

9:40am **MN-MoM5 Quantitative Work-of-Adhesion Values for use as an In-Fab Monitor of Stiction***, E.J. Thoreson,* Worcester Polytechnic Institute*; J. Martin,* Analog Devices, Inc.*;* ***N.A. Burnham,*** Worcester Polytechnic Institute

The Atomic Force Microscope (AFM), a common tool in the fab, can measure the work of adhesion between AFM tips and MEMS surfaces, which could become an eventual predictor of device stiction and failure. The goal of our study was to ensure reliable and quantitative values for the work of adhesion, i.e., the adhesive ("pull-off") force normalized for tip radius. Seventeen tips of four different types were used, with radii from 200 nm to 60µm, covering the range of typical MEMS contacts. The samples were unpatterned amorphous silicon dioxide MEMS die with two types of surface conditions (untreated and treated with a few angstroms of vapor deposited diphenylsiloxane). The cantilever's length, angle of repose, the radius and height of the tip, and the surface roughness all contribute to the measured pull-off force and work of adhesion. A simple correction for the surface roughness resulted in the expected linear dependence of pull-off force on radius, but the magnitudes for the pull-off force and work of adhesion were higher than expected. Normal heat-treated AFM tips have minimal surface roughness and result in magnitudes that are more reliable. The typical relative standard deviation and current relative uncertainty for these data are 20% and 15%, respectively. In this presentation, we derive how the cantilever and tip parameters contribute to the measured work of adhesion, show how the corrected results compare with theory, and list our recommendations for using the AFM as a quantitative in-fab stiction monitor. Work-of-adhesion data can now be meaningfully compared to actual device performance.

10:00am **MN-MoM6 An SPM-Based System for Contact Reliability Characterization***,* ***L. Chen,*** *N. McGruer, G. Adams,* Northeastern University*; R. Coutu, K. Leedy,* Air Force Research Laboratory

An SPM-based test station has been established for studying reliability physics of contacts in a micromechanical switch. A wide contact force range is accessible, from nN to mN, as determined by the mechanical properties of the microfabricated contact test cantilevers. During testing the contact force, the contact adhesion, and the contact resistance are measured. Material transfer is observed with an SEM. The cycling rate can reach 200 kHz by driving a piezo actuator at resonance. The contact properties of gold, ruthenium, rhodium and platinum and gold alloy have been studied and compared. Gold-on-gold contacts typically show decreased resistance, increased adhesion, and large amount of material transfer as the number of cycles increases. Ruthenium-on-gold and ruthenium-on-ruthenium contacts have better mechanical performance, but a higher contact resistance which increases with cycling. Two different shaped contacts, flat-top and hemispherical shaped, are used to study mechanical contact degradation. This work was supported by DARPA under its HERMIT program through research grant F33615-03-1-7002 to Northeastern University.

10:20am **MN-MoM7 Surface Chemistry of Organosilanes as a Vapor Phase Lubricant for Si-based MEMS Applications***, **D. Kim**, A.J. Gellman,* Carnegie Mellon University

Microelectromechanical systems (MEMS) offer the opportunity to improve a number of technologies and to develop devices that are significantly smaller and more lightweight than those in current use. Unfortunately, the long term operation of MEMS devices requires some form of lubrication for components in sliding contact. While traditional liquid lubricants cannot be used, vapor phase lubrication may be an effective solution. MEMS devices are made from single-crystal silicon and polycrystalline silicon, the surfaces of which are covered with a thin film of silicon dioxide, SiO@sub 2@, when exposed to air. The lubrication of MEMS materials requires both the replenishment of SiO@sub 2@ from the worn surfaces and the application of a lubricant film that will minimize wear. Organosilanes, R@sub n@Si(OR)@sub 4-n@, such as triethoxyphenylsilane, (C@sub 6@H@sub 5@)Si(OCH@sub 2@CH@sub 3@)@sub 3@, are proposed as vapor phase lubricants that can perform both functions. The surface chemistry of triethoxyphenylsilane on Si(100) and SiO@sub 2@ surfaces has been studied, using temperature programmed reaction spectroscopy and Auger electron spectroscopy. This chemistry was compared to that of tetraethoxysilane, (CH@sub 3@CH@sub 2@O)@sub 4@Si, which is widely used as a precursor for SiO@sub 2@ film deposition. Triethoxyphenylsilane decomposed readily, depositing SiO@sub 2@ and graphitic carbon on Si(100) and SiO@sub 2@ surfaces. Triethoxyphenylsilane formed more graphitic surface films than tetraethoxysilane on Si(100) surface at T=300-600 K. Triethoxyphenylsilane decomposes by C-O cleavage to ethyl groups which desorb as ethylene via @beta@ -hydride elimination. The remainder produces phenyl groups which desorb as benzene or decompose further to deposit graphitic carbon onto the surface. These results suggest that lubrication of MEMS materials could be accomplished, using vapor phase organosilanes such as triethoxyphenylsilane.

10:40am **MN-MoM8 Post-Processing Curvature Modification of Cantilever Microbolometer Focal Plane Arrays***, **S. Huang**, X. Zhang,* Boston University

Infrared vision is a key technology in a variety of military and civilian applications. Recent advances in MEMS have led to the development of uncooled microcantilever bolometers, which function based on the bending of bimaterial cantilevers upon the absorption of IR energy. Such microbolometer FPAs, however, always curve up or down because of the imbalanced residual stresses in the dissimilar materials, significantly weakening their performance and functionality. We report a post-processing engineering approach to address this issue: the method we used includes a combination of ion beam machining and rapid thermal annealing treatments. In our experiments, bimaterial SiNx/Al for microbolometers were fabricated using the surface micromachining technique with the polyimide as sacrificial material. The Al layer was deposited by electron beam deposition and the SiNx layer by PECVD. The thickness of the Al layer was 200 nm and that of the SiNx layer was 250 nm. To modify the curvature of the as-fabricated FPAs, first, ion beam machining was used. We found 20-min machining resulted in a significant improvement in the FPAs curvatures. Second, RTA was adopted to further modify the residual stresses and hence the curvatures of the FPAs. The FPAs initially bent down to the substrate, totally losing their function. A 5-min RTA treatment at 350Â°C resulted in less deflected pixels, while a treatment at 375Â°C led to pixels with an acceptable curvature. High-temperature, however, could deteriorate the residual stress state, causing the FPAs bent even upwards. In summary, we demonstrated that a combination of ion beam machining and RTA techniques can be used effectively to eliminate the residual stress-induced curvatures in cantilever microbolometer FPAs. Such an engineering approach also shines a light on a certain possibility to control "unwanted" initial curvatures in many other kinds of free-standing MEMS structures, such as micromirror arrays.

11:00am **MN-MoM9 Using Geometric Moiré to Measure the Deformation in Polymeric Nanostructures***, **Y. Zhao**, X. Zhang,* Boston University

This paper demonstrates a novel approach to measure the deformations in polymeric nanostructures. To our knowledge, it is the first effort to use geometric moiré technique into polymeric nanostructures. This approach has significance in the development of various biological microsystems comprising polymeric components, especially where they serve as mechanical sensors. The application of polymer material has recently extended to mechanical sensors, which measure forces on the order of nN or even smaller. Since many polymer used for this application is transparent and not compatible for electronic read-out, current approaches for deformation measurement are mainly based on direct optical observation. However, this approach is no long appropriate for nanostructures because the nanoscale deformation can hardly be resolved optically. In this work, geometric moiré recognition was utilized by interference between the polymer nanostructures and the scanning raster of the imaging system. A PDMS substrate with nanostructures was fabricated through a nanoimprinting process. The deformation is induced by thermal expansion of the polymeric substrate upon heating. The image of the nanostructures was taken by a CCD camera and transferred to a computer for data analysis. The deformation in nanostructures can thus be predicted. The results show that although the individual nanostructures can not be clearly viewed, the geometric moiré fringes by the interference between the polymeric nanostructures and the scan raster of the scanning imaging system can be obtained by adjusting the magnification. The moiré fringes amplify the tiny dimensional changes in the nanostructures (about 6nm between neighboring structures) as the form of pitch change or rotation of the fringes. Therefore, the deformation due to the thermal expansion can be predicted with a given temperature change, which is on the order of nanometer and can not be resolved by direct optical observation.

11:20am **MN-MoM10 High Sensitivity and Broad Dynamic Range MEMS Humidity Sensor***, A. Zribi, **W.-C. Tian**, A. Knobloch,* GE Global Research Center

A new design concept of a high sensitivity and broad dynamic range MEMS-based humidity sensor is introduced in this work. A simple MEMS structure combined with ultra thin films of polystyrene sulfonic acid (PSSA, H+) is operated in two different transduction modes to enable moisture detection within the entire range -60 to 25°C Dew Point (DP), i.e. 0.04 to 100% RH (assuming an ambient temperature of 25°C). The transducer comprises two identical freestanding silicon nitride membranes and micro-conductors patterned into various geometries on top of these membranes. Only one of the two membranes is coated with a 50 to 200 nm-thick PSSA film. When used in resonant mode, the MEMS transducer is sensitive to mechanical outputs from the PSSA film (gravimetric and stress/strain) and the overall sensor output is a shift in the resonant frequency of the nitride membrane. These high performance resonant sensors provide high resolution (2 ppm), low non-linearity (0.14%), low hysteresis (0.07%) and high sensitivity (70 Hz/°C DP) and is designed for moisture detection between 0.04 and 50% RH. However, when operated in calorimetric mode, the differential heating power induced by the heat of adsorption/desorption of moisture from the PSSA film is used to measure moisture between 50 and 100% RH. The PSSA adsorbent transfer function for thermal and mechanical transductions are analyzed in this work. We will also discuss the design, modeling, and optimization of the transducer in both operational modes and the advantages of this design approach over the state of the art in terms of performance and reliability.

11:40am **MN-MoM11 Vacuum Packaging MEMS Devices***, R. Patel, M.U. Pralle, E.A. Johnson, **A.C. Greenwald**,* Ion Optics, Inc.

MEMS devices have unique packaging considerations to allow for mechanical motion. Vacuum packaging is required to reduce atmospheric drag for high frequency motion, to reduce thermal convection, etc. To achieve stable low pressures material selection is of paramount importance. Low temperature options are not suitable for very long-term reliability so that sealing materials are limited to impervious ceramics or metallic composites. Ion Optics has developed a MOEMS infrared gas sensor using photonic crystal technology.@footnote 1@ Operation requires a high temperature thermally isolated filament and vacuum packaging. Experiments in vacuum packaging this device have been performed for both single die in leadless chip carriers (LCC) and with wafer level packaging (WLP). Both low-melting point solders and ceramic frits have been tested for sealing. Different getter materials to reduce initial pressure and improve long-term reliability were also tested. The electrical performance of the heater is a sensitive function of package pressure.@footnote 2@ Devices were calibrated prior to sealing and then used as gauges to measure internal package pressure during the sealing and operation. Pressures down to 10mtorr were achieved. Process optimization studies included time-temperature profiles for bake-out using an RGA to study gas evolution from package and chip materials. Additional post-sealing studies broke packages in a sealed chamber and measured evolved gas composition and volume. Despite pre-bakeout at over 200C, water vapor was the highest volume gas retained/evolved, followed by oxygen, carbon dioxide and nitrogen. The minimum pressures attained in WLP were lower than that for LCC. @FootnoteText@ @footnote 1@ Nicholas Moelders, et. al., Mat. Res. Soc. Symp. Proc. Vol. 729, paper U5.2(2003).@footnote 2@ Nicholas Moelders et. al., Mat. Res. Soc. Symp. Proc. Vol. 782 paper A5.32(2004).

Nanometer-Scale Science and Technology
Room 204 - Session NS1-MoM

Nanometer Scale Structures

Moderator: S.V. Kalinin, Oak Ridge National Laboratory

8:20am **NS1-MoM1 Morphological Control of Nanoporous Gold by Surfactants*, J. Biener,*** Lawrence Livermore National Laboratory*; M.M. Biener,* Harvard University*; T. Nowitzki,* Universitaet Bremen, Germany*; A.V. Hamza,* Lawrence Livermore National Laboratory*; C.M. Friend,* Harvard University*; M. Baeumer,* Universitaet Bremen, Germany

Nanoporous Au (np-Au) prepared by electrochemically-driven dealloying of Ag-Au alloys has attracted considerable interest due to potential sensor and actuator applications. The material exhibits an open sponge-like morphology of interconnecting ligaments on the nanometer length scale. Due to the very high surface-to-volume ratio of np-Au, the surface chemistry should play an important role in controlling the pattern formation during dealloying. Ion-bombardment of Au surfaces can be used as a model system to study the mechanisms of pattern formation during dealloying: Both processes generate a supersaturation of Au adatoms and vacancies, which in turn results in the nucleation of Au adatom clusters and vacancy islands. The actual morphology evolving under these conditions strongly depends on the mobility of vacancies and adatoms, and in particular on the stabilization of undercoordinated Au atoms by adsorbate species. Here, we report on oxygen and argon ion sputter experiments on Au(111) surfaces which allow us to study the influence of oxygen adsorption on pattern formation. The resulting surface morphologies were characterized by scanning tunnelling microscopy (STM), and the amount of adsorbed oxygen was measured by X-ray photoemission spectroscopy (XPS). Specifically, our experiments demonstrate that adsorbed oxygen stabilizes a rougher surface morphology by stabilizing undercoordinated Au atoms. Our results thus open a new door to control the morphology of nanoporous metals by means of surfactants. 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.

8:40am **NS1-MoM2 Characterization of Polymer Nanostructures Deposited with Thermal DPN*, A.R. Laracuente,*** *M. Yang, P.E. Sheehan,* Naval Research Laboratory*; W.P. King,* Georgia Institute of Technology*; L.J. Whitman,* Naval Research Laboratory

We have developed a new variant of dip-pen nanolithography (DPN) called thermal DPN (tDPN),@footnote 1@ where a heated atomic force microscope cantilever controls the deposition of a solid "ink." Using this technique we have successfully deposited semiconductors, insulators, and metals, and extended it into UHV. As an example, we have deposited poly(3-dodecylthiophene) (PDDT), a polymer that shows great promise as an active component in organic electronic devices. PDDT nanostructures with lateral dimensions below 100 nm have been written on silicon oxide and gold surfaces. Using a unique UHV instrument that combines a scanning electron microsope (SEM), a scanning Auger, and in-situ four-probe measurements, we have characterized PPDT nanostructures written across prefabricated Au electrodes. I-V measurements show the nanostructures to be initially insulating (>10G@ohm@); however, the resistance unexpectedly drops several orders of magnitude (to as low as 33 k@ohm@) upon prolonged exposure to the SEM electron beam. When the beam is turned off, the resistance gradually increases (~1 G@ohm@/day). We have also found that a high resistance state can be restored by exposure to H@sub 2@, suggesting that the polymer film is not damaged by the electron beam, but rather that charged H vacancies are generated in the PPDT film by the high-energy electrons, and that the vacancies can be reversibly filled by H@sub 2@ exposure. @FootnoteText@ @footnote 1@ P. E. Sheehan, et al., Appl. Phys. Lett. 85, 1589 (2004).

9:00am **NS1-MoM3 Growth Modification of Ferromagnetic Core-Shell Nanomaterials by a Magnetic Field*, K.T. Leung,*** University of Waterloo, Canada

Our recent work on metal nanoparticles (Cu, Ni, Co) electrochemically deposited on an ultrathin polypyrrole film grown on a gold-coated silicon electrode shows that the morphology (size, shape, density and distribution) of these nanostructured materials can be easily controlled by varying the wet deposition conditions (pH, electrolyte concentration, deposition potential, charge, and current density), and the thickness and morphology of the polypyrrole film. Using similar electrochemical techniques, we have recently obtained mono-sized, uniformly distributed Fe core-shell nanoparticles with two different morphologies: quantum dots of 4-10 nm in diameter and 20x110 nm "nano-surfboards" (<5 nm thick). These nanoparticles are found to primarily consist of a Fe metallic core and a mixed Fe oxides shell (2-3 nm thick). In the present work, we report the first evidence of morphological changes induced by an external magnetic field during growth. Implications of constructing patterned nanostructured materials using this technique will also be discussed. @FootnoteText@ * Work supported by the Natural Sciences and Engineering Research Council of Canada.

9:20am **NS1-MoM4 Fabrication of Defect-free Sub-10nm Si Nanocolumn using Cl Neutral Beam*, J.K. Chen,*** *T. Kubota,* Tohoku University, Japan*; U. Uraoka, T. Fuyuki,* Nara Institute of Science and Technology, Japan*; I. Yamashita,* Matsushita Electric Industrial Co., Ltd., Japan*; S. Samukawa,* Tohoku University, Japan

We fabricated nanocolumn structure by using a low energy Cl neutral beam and a ferritin iron-core mask. By optimizing beam accelerated energy, extremely high etching selectivity of Si to ferritin iron core masks as well as highly anisotropic etching profile could be realized. As a result, the diameter of the Si nanocolumn structure was 7 nm, which was identical to that of the iron core in the ferritin. We were also able to achieve an extremely high aspect ratio of about 19 (hight: 130nm) with maintaining the diameter of 7nm. Additionally, the crystal defects of 7nm Si nanocolumn were observed by using TEM images. We found that defect-free Si nanocolumn etching could be accomplished by using the Cl neutral beam. It is much difficult for conventional plasma etching processes to fabricate such fine structure, because the high-energy photons in the plasma cause low etching selectivity to the iron core mask and generate crystal defects in the silicon.

9:40am **NS1-MoM5 Three-Dimensional Nanochannels Formed by Oxide Deposition and Fast Etching of Polymer*, C. Peng,*** *S.W. Pang,* University of Michigan-Ann Arbor

Nanochannels are widely used in biomedical applications such as DNA analysis and biomolecule detection. We report a method using sacrificial polymer and oxide to form three-dimensional (3D) nanochannels. Polymer nanostructures were patterned on Si substrates using optical lithography or nanoimprint lithography, followed by oxide deposition to form the sealed channels. A high-speed dry etching technique for removing the sacrificial polymer was developed using an oxygen plasma at high power, high pressure, and elevated temperature. This dry etching technique provides a fast lateral etch rate of 3.91 µm/min for the polymer inside nanochannels, which is an order higher than conventional reactive ion etching. High selectivity of 1200 is obtained between the lateral etch rate of polymer inside the nanochannels and the vertical etch rate of oxide. Etch rate dependence on pressure, temperature, and channel width were studied. It was found that the etch rate increases with pressure and temperature. To form multiple levels of nanochannels, the oxide covering the channels was planarized by a photoresist coating and etch-back process. After oxide planarization, the channel formation process is repeated and multiple levels of nanochannels can be stacked to build 3D nanostructures. A two-level nanochannel structure has been demonstrated and more complex 3D system is developed. Since oxide is transparent to visible light and the channels have hydrophilic surfaces, such 3D nanofluidic system is suitable for various biomedical studies.

10:00am **NS1-MoM6 Chemical Vapor Deposition onto Size-Selected, Aerosolized Silicon Nanoparticles*, J.T. Roberts,*** *J. Holm, Y.-C. Liao, A. Nienow,* University of Minnesota

We describe a method for depositing metal oxide layers onto the surfaces of aerosolized nanoparticles. Chemical vapor deposition was used to deposit group IV metal oxides, including zirconium dioxide, onto silicon.

The film precursors were anhydrous metal nitrates. Layers were deposited on silicon particles of initial diameter between 10 and 20 nm. The results are important because they describe a new approach for manipulating interfacial properties of nanoparticles that have materials applications. More fundamentally, the results are among the first kinetic and mechanistic studies of surface reactivity in aerosolized nanoparticles. Deposition was investigated using tandem differential mobility analysis (T-DMA) and transmission electron microscopy (TEM). Aerosolized, crystalline silicon nanoparticles were extracted from a plasma synthesis chamber into an atmospheric pressure flow tube reactor. The particle streams were sent through a furnace for thermal activation, through a bipolar diffusion charger to establish a known charge distribution on the particles, and then through a differential mobility analyzer (DMA-1). DMA-1 was used to create a stream of monodisperse particles; selected diameters were in the 10-20 nm range The monodisperse particle streams were swept into a reaction zone, which was a heated copper tube with a valve for the precursor introduction. The reaction zone was designed for maximal flexibility, with variable temperature (25-200 ÂºC), particle residence time (1-10 s), and gas-phase composition. Particles that exited the reaction zone were analyzed in two ways: (1) for size changes, with a second DMA capable of measuring diameter changes as small as 1%, and (2) for morphological changes that are induced by deposition, using TEM.

10:20am **NS1-MoM7 The Electronic Structure of Diamondoids Measured with Synchrotron Radiation***, **T.M. Willey,*** Lawrence Livermore National Laboratory*; C. Bostedt,* Technische Universität Berlin, Germany*; T. van Buuren,* Lawrence Livermore National Laboratory*; J.E. Dahl, S.G. Liu, R.M.K. Carlson,* MolecularDiamond Technologies, Chevron Texaco*; T. Möller,* Technische Universität Berlin, Germany*; L.J. Terminello,* Lawrence Livermore National Laboratory

Although the Group IV semiconductors Si and Ge show quantum confinement effects in nanoparticles, diamond particles a few nanometers in size do not show this increase in band-gap. However, various calculations on diamond predict increasing HOMO-LUMO gap as the diameter decreases below 1 nm. We have tested this hypothesis and will present the first measurements of the electronic structure of diamond in this near- and sub- nanometer size regime using synchrotron radiation techniques. Pure, defect-free, hydrogen-terminated diamondoids were investigated in the gas phase to eliminate particle-particle interaction and ensure measurement of pristine molecules. X-ray absorption probes the unoccupied electronic states; the carbon K-edge reveals rich electronic structure in these materials. We will present our analysis showing the emergence of a diamond-like band structure and a comparison to the predicted change in HOMO-LUMO gap from several calculations and our own recent X-ray absorption and emission measurements on solid-state diamondoids.

10:40am **NS1-MoM8 Low Temperature Melting of Tungsten and Ruthenium Nanorod Arrays***, **T. Karabacak,** D.-X. Ye, P.-I. Wang, G.-C. Wang, T.-M. Lu,* Rensselaer Polytechnic Institute

We observed that tungsten and ruthenium nanorod arrays melted at ~30% and ~40% of their bulk melting points (W at 3410 °C and Ru at 2334 °C), respectively. These findings reveal the most dramatic reduction in the melting temperature of nanostructures ever reported in literature. The W and Ru nanorods were grown by an oblique angle sputter deposition technique through a physical self-assembly mechanism due to the shadowing effect. The W nanorods have an average width of ~75 nm and an average length of ~500 nm and the Ru nanorods have an average width of ~75 nm and an average length of ~370 nm. These nanorods were isolated from each other with gaps ~20 nm. The nanorods were vacuum-annealed at various temperatures in the range of 700-1000 °C for 30 minutes at each annealing temperature. The melting process was investigated through the analysis of scanning electron microscopy (SEM) images and X-ray diffraction (XRD) spectra. W and Ru nanorods started to coalesce and formed continuous films at temperatures ~1000 °C and ~950 °C, respectively. In addition, the melting was associated with recrystallization as observed from XRD spectra. After melting, W rods transformed from metastable cubic @beta@(200) phase to bcc @alpha@(110) and Ru rods changed their texture from hcp(100) to a mixture of (002) and (101) crystal orientations. The low temperature melting of the nanorods is explained to be mainly due to their small size and increased surface/volume ratio, which results in the "premelting". The premelting is believed to be further enhanced by the presence of interstitials (due to the atomic peening of energetic Ar, W, or Ru particles of tens of eV) or impurity (O in the case of @beta@-W rods) atoms in the lattice structure of the rods accompanied during sputter deposition.

11:00am **NS1-MoM9 Self-Assembly and Photoluminescence of CdSe Quantum Dots from Buffer-Layer-Assisted Growth***, **V.N. Antonov,** P. Swaminathan, J.S. Palmer, J.H. Weaver,* University of Illinois at Urbana-Champaign

Nano-particles of II-VI semiconductors (qantum dots) exhibit well-known size-dependent optical properties due to the quantum confinement of their charge carriers. The principal routes of their synthesis have been chemical and thus difficult to integrate with silicon technology. In this paper, we demonstrate that CdSe quantum dots can be self-assembled and delivered on almost any substrate with the help of buffer-layer-assisted growth (BLAG). In BLAG, physical vapor deposition of atoms or molecules on multilayers of van der Waals solids leads to spontaneous formation of clusters. Subsequent warm-up and desorption of the buffer causes the clusters to diffuse and aggregate into larger structures. The extent of this aggregation is controlled by the thickness of the buffer. Here, sub-monolayer depositions of CdSe on Xe buffers ranging from 4 to 35 ML result in formation of quantum dots ranging from small 2 nm clusters to extended ramified islands with typical branch width of 3 nm. The diffusivity of CdSe nano-particles on solid Xe is determined from the evolution of particle density with buffer thickness. The photoluminescence spectra of the CdSe dots are measured at 3 K, and their maxima shift through a large portion of the visible range with particle size. The spectra are analyzed in terms of the measured size distributions of the dots and the existing models of quantum confinement in CdSe. BLAG should be applicable for the synthesis of quantum dots of any II-VI semiconductor on almost any substrate.

11:20am **NS1-MoM10 Comparative Study of ZnO Nanorods Grown by MOCVD and Solution Method***, **Y. Tak**, K. Yong,* POSTECH, Korea

ZnO nanomaterials have been intensively studied due to their characteristic properties and possible applications in nano-device fabrication. Various synthesis techniques of ZnO nanomaterials have been developed such as vapor liquid solid (VLS) method, metalorganic chemical vapor deposition (MOCVD), physical vapor deposition (PVD) and solution method. Among these methods, MOCVD and solution method can be easily applicable to low temperature process. We report on the comparative study regarding characteristics of ZnO nanorods grown by MOCVD and solution method, respectively. For MOCVD growth of ZnO nanorods on silicon, diethylzinc(DEZn) and oxygen were used as reactants. The growth temperature was 400 ~ 500@super o@C and thin ZnO layer was used as a buffer layer. For solution method, Zn or ZnO coated silicon substrate was placed in a solution containing Zn(NO@sub 3@)@sub 2@ and hexamethylenetetramine (HMT) or ammonia water. The reaction temperature and time were 60 ~ 90 @super o@C and 6h, respectively. Large quantities of well-aligned ZnO nanorod could be prepared by both MOCVD and solution method. The morphology and crystallinity of the samples grown by two different methods were compared using field-emission scanning electron microscopy (FE-SEM) and X-ray diffraction spectroscopy (XRD). High-resolution transmission electron microscopy (HR-TEM) and X-ray photoelectron spectroscopy (XPS) were used to analyze atomic structures and element composition. Photoluminescence properties of the samples were compared using He-Cd (325nm wavelength) laser as an excitation source.

11:40am **NS1-MoM11 Heat Conduction across Nanolaminates of Alternating Metal-Dielectric Materials***, **Y.S. Ju**,* UCLA

High density of interfaces can strongly impede heat conduction across nanolaminates. This can be exploited to create superior thermal barrier coatings without compromising mechanical or chemical protection characteristics. Thermal barrier coatings are critical elements that help reduce power requirements of solid-state phase change memory devices and thermally assisted magnetic recording media. Previous theoretical and experimental studies have improved our understanding of the thermal interface resistance. Significant discrepancy, however, still exists between theoretical predictions and experimental data at elevated temperatures. We will present experimental and theoretical studies of energy transport across interfaces between nanoscale metal and dielectric thin films. We will describe details of sample preparation and data analysis procedures we developed to address challenges involved in accurate measurements. The thermal interface resistance between Ta and amorphous AlOx is found to be considerably smaller than previously reported values for comparable metal-dielectric interfaces, which suggest that the intrinsic interface resistance is closer to the model prediction than previously suggested. We also report the thermal resistance of nanolaminates consisting of alternating layers of metal and dielectric materials. The thermal conductivity of the nanolaminates is found to be well-below the minimum thermal conductivity limit of each component and is consistent with our single interface thermal resistance data. We will also describe a continuum two-fluid model we develop to examine the impact of spatial non-equilibrium between electron and phonon on the thermal resistance of nanolaminates. Fundamental understanding of nanoscale energy transport across interfaces will allow systematic design and engineering of interfaces to either enhance or suppress heat conduction in nanolaminates.

Nanometer-Scale Science and Technology
Room 210 - Session NS2-MoM

Nanowires

Moderator: C.R. Marrian, IBM

8:20am **NS2-MoM1 Probing Growth Defects Inside Nanowires***, **J. Eriksson**, A. Mikkelsen, E. Lundgren,* Lund University, Sweden*; W. Hofer,* University of Liverpool, U.K.*; N. Skold, L. Samulesson, W. Seifert,* Lund University, Sweden

Free-standing semiconductor nanowires are perceived as future components in nanoelectronics and photonics. In fact, applications such as for example, bio/chemical sensors, n- p- type diode logic and single nanowire lasers have already been realized in the laboratory.@footnote 1@ Because of the extremely small dimensions of a nanowire, atomic scale structural features can have a significant impact on their properties. As a result, structural methods that address all these issues are highly desirable. Recently we have demonstrated a new method to image individual atoms inside III-V semiconductor nanowires using a combination of STM and a novel embedding scheme.@footnote 2@ In this way, we are able to image areas of the nanowire with atomic resolution both along the wire, and through the face of the wire. In this contribution we present a cross-sectional STM study of the structure and the electronic properties of stacking faults inside a GaAs nanowire containing an embedded GaInAs segment. The stacking faults are created due the formation of twins as the nanowire is grown. Spectroscopy measurements performed directly on a stacking fault are compared to density functional theory calculations, and the influence of the stacking fault on the electronic properties of the wire will be discussed. @FootnoteText@@footnote 1@L. Samuelson, Mater. Today 6 (2003) 22. @footnote 2@A. Mikkelsen et al, Nature Materials. 3 (2004) 519.

8:40am **NS2-MoM2 Optical Activation of Implanted Impurities in ZnS Nanowires***, D. Stichtenoth, D. Schwen, S. Mueller, C. Borchers, **C. Ronning**,* University of Goettingen, Germany

Nanostructures of zinc sulfide (ZnS), a II-VI compound semiconductors with a direct band-gap of 3.66 eV in the cubic phase and 3.74 eV in the wurtzite phase, show interesting optical properties, making it a promising candidate for optoelectronic devices. Single crystalline nanobelts and -wires were synthesized in a computer-controlled process according to the VLS mechanism. We investigated the morphology, structure and composition by scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), and X-ray diffraction (XRD). The optical properties have been studied by temperature dependent photo- (PL) and cathodoluminescence (CL). The synthesized ZnS nanowires were implanted with nitrogen and boron as potential donor and acceptor, respectively. The implanted nanowires were investigated directly after ion implantation and showed a high quantity of defects resulting into non-luminescence material. Annealing procedures recovered the crystal structure and the optical properties, and we found varying and new PL-lines indicating the activation of the implanted impurities.

9:00am **NS2-MoM3 Metal, and Conducting Polymer Nanowires for Gas and Biomolecule Sensing***, **M. Yun**,* University of Pittsburgh*; C. Lee, R. Vasquez,* Jet Propulsion Laboratory*; N. Myung,* University of California at Riverside*; J. Wang, H. Monbouquette,* University of California at Los Angeles*; A. Mulchandani,* University of California at Riverside

Single Palladium (Pd), Polyaniline(PANI), and Polypyrrole(PPY) nanowires from 70 nm to 300 nm in diameter and up to 7 Âµ in length have been synthesized using e-beam lithography and electrodeposition. This fabrication method enables the use of various materials for single nanowire sensors, such as polymers, metal oxides, and semiconductors. These fabricated Pd nanowires are used to sense hydrogen gases and have achieved a sensitivity of 0.02% H2. In addition, we have observed that the resistance of the 200 nm wide avidin-functionalized PPY nanowires increased rapidly to a constant value upon addition of 1 nM of the biotin-DNA conjugate and the resistance increased with increasing concentrations up to 100 nM. At last, we will present that arrays of nanowires with controlled dimensions are fabricated on substrates, optionally as integral parts of multilayer structures, by means of a high-yield process based on ion milling on steps (IMOS). To demonstrate the utility of functionalized IMOS nanowires as sensors, we have successfully demonstrated Pt nanowire array and precisely assembled glucose oxide (GOx) on Pt nanowire array by co-deposition with electropolymerized PPY. A mixture of GOx and pyrrole is used in PBS solution for electrochemical polymer formation and GOx immobilization. It has been verified by measuring the current sensitivity of 0.3 nA/mM to the glucose with IMOS Pt nanowires.

9:20am **NS2-MoM4 Determination of the Mechanical and Electromechanical Properties of 1D-nanostructures***, **A. Heidelberg**, B. Wu, J.G. Sheridan, J.J. Boland,* Trinity College Dublin, Ireland

Nanowires (NWs) have attracted considerable interest as nanoscale interconnects and as the active components of both electronic and electromechanical devices. Nanomechanical and nanoelectromechanical measurements are a challenge but remain key to the development and processing of novel NW-based devices. Here, we report a general method to measure the spectrum of NW mechanical properties based on NW bending under the lateral load from an atomic force microscope (AFM) tip.@footnote 1@ For electromechanical measurements bending experiments have been carried out with simultaneous measurement of the N@aa W@s conductivity. Mechanical measurements on Li@super +@(Mo@sub 3@Se@sub 3@)@super -@ NW bundles@footnote 2@ with a diameter range between 25 and 200 nm have been carried out using a SPM-nanomanipulator. In these experiments NWs were deposited out of solution across trenches on SiO@sub 2@. To prevent any slippage of the NWs during the manipulation, they were pinned down by E-beam induced deposition of Pt at the trench edges in a dual beam FIB/SEM system. Taking into account the wire shape and dimensions as well as the AFM cantilever dimensions, the Youngs modulus and the maximum bending strength of the NWs can be calculated from the force-displacement traces obtained by the lateral manipulations. The Youngs modulus for Li@super +@(Mo@sub 3@Se@sub 3@)@super -@ NWs shows a strong radius dependence. It increases exponentially with decreasing NW diameter which can be attributed to shear effects between the individual NWs in the NW bundles. For NWs with a radius of 30 nm a modulus of 1.22 TPa is found. The NWs show brittle failure and the bending strength increases with decreasing wire radius. Electromechanical properties of NW bundles were also measured and compared to data obtained on metallic (Au, Cu) and semiconducting (Si) NWs. @FootnoteText@ @footnote 1@B. Wu, A. Heidelberg, J. J. Boland, Nat. Mater. (accepted)@footnote 2@A. Heidelberg et al., Z. Phys. Chem. 217 (2003) 573.

9:40am **NS2-MoM5 Nanowires: From Biological Sensing to Computing and Much More!***, C.M. Lieber, **C. Yang**,* Harvard University **INVITED**

Nanotechnology offers the promise of producing revolutionary advances in many areas, extending from biology and medicine to electronics and computing, and thus may impact in a substantial way our future lives. This presentation will provide an overview to the bottom-up paradigm for nanotechnology enabled using nanowire building blocks. First, the growth of nanowires, with composition controlled down to the atomic scale, their fundamental electronic properties, and parallel assembly and interconnection will be described. Second, nanowire devices configured as electrically-based biosensors will be discussed with an emphasis on disease detection and ultimate sensitivity limits of these nanodevices, as well as the potential linkage to hybrid information processing systems. Third, studies of nanowire based electronic circuits and nanocomputing systems will be critically examined. Lastly, challenges that must be met to realize these and other nanotechnologies in the future will be summarized.

10:20am **NS2-MoM7 Direct Atomically Resolved Imaging of Nanowire Heterostructures and Nanowire Substrate Interaction***, **A. Mikkelsen**,* Lund Universty, Sweden*; J. Eriksson, L. Ouattara, E. Lundgren,* Lund University, Sweden*; T. Knaapen,* Eindhoven Technical University, The Netherlands*; N. Skold, W. Seifert, L. Samuelson,* Lund University, Sweden

Self-assembled semiconductor nanowires are a among the most interesting systems for doing low dimensional physics, as well as for realizing many future electronic and optoelectronic devices.@footnote 1@ Due to efficient strain relaxation a wide range of heterostructures, not possible in the bulk, can be grown in nanowires, and as a result, a multitude of complex nanowire based heterostructure devices has been realized in recent year. Very recently it has even been possible to grow optically active III-V structures on Silicon substrates.@footnote 2@ Because of the seeding type growth process of the wires, it is further possible to grow the wires by self-assembly in well defined positions for example on a chip. Using Scanning Tunneling Microscopy (STM), we address both the issue of heterostructure growth, the initial growth of the nanowire on the substrate and the influence of nanowire growth on the substrates - with atomic scale resolution. We apply our newly developed scheme to image individual atoms inside III-V semiconductor nanowires using a combination of STM and embedding.@footnote 3@ Using this method we have imaged GaInAs segments in GaAs wires with atomic resolution. We show that while the GaInAs segments are in principle perfectly defined on the atomic scale, an In distribution exists above the segment and also on the side facets of the wire. We further image GaAs nanowires at the GaAs(001) substrate interface, revealing intriguing details about both the initial growth of the nanowire along the surface, and the subsequent growth of the out-of-plane free standing wire. Finally we have investigated the influence of the nanowire growth, by Au seed particles, on the surrounding substrate - revealing that significant structural changes can occur. @FootnoteText@ @footnote 1@ L. Samuelson, Mater. Today 6 (2003) 22.@footnote 2@ T. Maartensson et al, Nano Lett 4 (2004) 1987@footnote 3@ A. Mikkelsen, et al, Nature Materials. 3 (2004) 519.

10:40am **NS2-MoM8 Near-field Scanning Photocurrent Microscopy of a Nanowire Photodetector***, **Y. Gu**, E.-S. Kwak, J.L. Lensch, J.E. Allen, T.W. Odom, L.J. Lauhon,* Northwestern University

One-dimensional nanomaterials such as semiconductor nanowires (NWs) are being considered for a variety of device technologies, including nanoscale photodetectors (PDs). The mechanisms of carrier photogeneration in nanoscale PDs have been addressed in a number of studies, but the charge transport and collection mechanisms have received comparatively little attention and are not well understood. In this regard, photoconductivity measurements with uniform illumination (spot size larger than the device) may be insufficient to establish the operational principles of NW devices because (1) the internal electric fields may be highly non-uniform, and (2) similarities between conventional and NW device characteristics may be fortuitous. To understand the global response and the ultimate potential of NW PDs, an understanding of the photoresponse on a smaller length-scale is desirable. We have developed a new technique, near-field scanning photocurrent microscopy (NSPM), to explore the local photoresponse of semiconductor NW devices. A near-field scanning optical microscope (NSOM) was used to image the photocurrent induced by local illumination (excitation spot size less than device size) along the length of a metal-semiconductor-metal (MSM) PD based on a single CdS NW. Under uniform monochromatic illumination, the MSM PDs exhibited photocurrents ~10@super 5@ larger than the dark current (< 2 pA). Under local illumination, the response of the devices was limited to regions near the M-S contact. Analysis of the spatial variation and bias dependence of the local photocurrent allowed the mechanisms of photocarrier transport and collection to be identified. The NSPM technique we describe can be readily extended to other NW-based devices with similar geometries, and provide insight into the operation principles of these devices. NSPM therefore has the potential to significantly advance the understanding and development of NW device technology.

11:00am **NS2-MoM9 Fabrication of Silicon Nanowires with Addressable Au-coated Si Islands***, **C. Wang**, K.S. Ma, M. Madou,* University of California, Irvine

With the increasing interest in various aspects of nano devices, it is becoming apparent that controlled growth is the key to manufacturing. The ability to control the growth of materials on the nanometer scale is important since it determines the device applications. Within many various material, Si nanowires (SiNWs) have attracted intensively research efforts in the synthesis and characterizations. The vapor-liquid-solid mechanism is the rife technique to growth SiNWs. The SiNWs were grown by decomposition of SiH4 as the Si atom sources. Most recently, the other approach, e.g. the solid-liquid-solid, has been developed. In this, the bulk Si wafers were used as either the substrates or Si sources. A thin Au layer was deposited on the substrate as catalyst. In this method, the SiNWs were directly deposited onto the conducting substrate. The post-growth processes are needed to employ those SiNWs as building blocks for the electronics. Herein, we report an alternative method to fabricate the SiNWs by adopting SLS mechanism. The addressable Au-coated Si islands were fabricated by lithography with lift-off on the SiO2 pre-coated substrate. The substrates were then heated to 900 ÂºC in N2/H2 gas. By this isolated Si islands technique, the grown SiNWs were settled down on the insulated substrate. By e-beam or optical lithography, the conducting electrodes can be fabricated on the wires. The islands are the starting point of the growth which can be served as the marker to localize the positions of SiNWs. By engineering design the size and position of the islands, the post-growth fabrication will be much easy instead of using alignment technique under the microscopes. We demonstrated a convenient technique to fabricate SiNWs of controllable position using SLS mechanism. The synthesized SiNWs were deposited on the non-conducting substrates. The widths of the wires are in the tens of nanometer range. The characterizations of synthesized SiNWs were carried out.

11:20am **NS2-MoM10 Mechanical and Electromechanical Properties of Metallic Nanowires***, **B. Wu**, A. Heidelberg, J.J. Boland,* Trinity College Dublin, Ireland

Here, we present a general method to measure the full spectrum of nanowire (NW) mechanical properties: ranging from Youngs modulus E, yield strength, plastic deformation and failure. This method is based on NW bending under the lateral load from an atomic force microscope tip, and involves the manipulation of NWs after they have been mechanically pinned at the edge of a trench using a focused ion-beam. We find that for Au and Cu NWs the Youngs modulus (E) is essentially independent of diameter, while the yield strength is largest for the smallest diameter wires, with strengths up to 100 times that of bulk materials and substantially larger than that reported for bulk nanocrystalline metals (BNMs). In contrast to BNMs, NW plasticity is characterized by strain-hardening demonstrating that dislocation motion and pile up is still operative down to diameters of 40 nm. Possible origins for the different mechanical properties of NWs and BNMs are discussed. The application of this method has also been extended to electrical measurement of NW systems under mechanical strain. For metallic and conducting polymer NWs, the resistance was monitored when NWs were subjected to loads by AFM tip. The potential applications will be discussed.

11:40am **NS2-MoM11 In Situ Resistance Measurement of Epitaxial Silicide Nanowires***, H. Okino, R. Hobara, Y. Hosomura, I. Matsuda, S. Hasegawa,* University of Tokyo, Japan*; **P.A. Bennett**,* Arizona State University

We present in situ resistance measurements for CoSi2 nanowires (NWs) on Si(110), using a custom-built multi-tip UHV-STM. We have shown elsewhere that self-assembled epitaxial silicide NWs can be formed with a variety of transition metals (Co, Ni, Fe, Ti, Pd, Dy) on Si(100), Si(111) or Si(110) surfaces, in various combinations (Phys. Rev. Lett v93, 2004, p256102). In most cases, these form via a new "endotaxial" growth mechanism, in which the silicide grows into the substrate along inclined Si{111} planes, breaking the symmetry of the surface and leading to the long, thin island shape. These NWs are metallic, single-crystal structures with potential applications as interconnects, nano-electrodes or as functional elements for nano-electronic devices. Four independent STM tips can be positioned to contact a single NW. Each tip is pushed ~ 10nm beyond the point of tunneling to make good electrical contact with the NW. Four-point measurements on a single NW yield typical values of 600 @ohm@ and 60 @ohm@ for the NW and contact resistance, respectively, for a NW with dimensions 60 nm wide, 40 nm high and 2 microns long. Similar values are obtained from a 2-point configuration by measuring the resistance vs. tip separation. The corresponding resistivity is @rho@ = 20-30 µ@ohm@cm, which is similar to that for high-quality epitaxial films of CoSi2 at 300K. This indicates that defect- and/or surface-scattering is small for these structures. We also find that the NWs are isolated from the substrate by a Schottky barrier with zero-bias resistance of ~ 10@super 7@ @ohm@. The good isolation results from a surface depletion layer near the NWs.

Plasma Science and Technology

Room 302 - Session PS-MoM

Plasma Diagnostics

Moderator: S.G. Walton, US Naval Research Laboratory

9:00am **PS-MoM3 Emissive Probes in Processing Plasmas - A Good Way to Measure the Plasma Potential***, **N. Hershkowitz**[1], D. Lee,* University of Wisconsin **INVITED**

Electron emissive probes can provide measurements of the plasma potential with potential resolution of 0.1 V and spatial resolution of 0.1 cm in low pressure DC Argon plasma. The plasma potential is an important parameter in processing plasmas. However, such plasmas present many challenges to the use of emissive probes including rf, reactive gases, plasma deposition, impurity generation and relatively high neutral pressure

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[1] **2004 Plasma Prize Winner**

so probes are rarely used. This talk provides experimental evidence that many of the challenges can be overcome and argues for increased use of emissive probes.

9:40am **PS-MoM5 A New Diagnostic Method of Radio-Frequency Plasmas Produced in Insulated Vessels*, H. Shindo,*** Tokai Univeristy, Japan

A new method to measure electron energy by an emissive probe has been proposed. The method is based on measurement of the functional relationship of the floating potential and the heating voltage of emissive probe. From the measured data of the floating potential change as a function of the heating voltage, the curve of the probe collection current-voltage can be analytically obtained. The present method has several important advantages of the following: (1) it is even applicable to radio-frequency plasma in which the potentials are usually fluctuating, (2) also applicable to plasmas which are produced in non-conductive containers. In the experiment, the emissive probe 30 micrometer diameter tungsten was heated by 40 kHz pulse voltage, and the floating potential at the heating voltage off period and the floating potentail difference between the heating off and on period were measured by digital oscilloscope in argon plasma. The measurements were made in both the capacitively coupled and inductively coupled plasmas. It was shown that the plasma electron energy probability function could be obtained without any RF compensating circuit even in capacitively coupled plasmas. In particular, since the method is very sensitive near the plasma potential, the clear indication for the depletion of the low energy electron could be obtained. This low energy electron depletion is due to high plasma potential. Therefore, in the inductively coupled plasma this low energy electron depletion was obtained near the induction antenna, but at the further positions from the antenna the energy distribution became Maxwellian. This feature has also been reported recently. This change in the electron energy distribution found in ICP was very systematic with the gas pressures and the distnaces from the antenna. Thus the present method is quite innovative in that it is applicable to the potential fluctuating RF plasma and measurements are all done in a floating condition of probe.

10:00am **PS-MoM6 Energy Dissipation in Capacitively Coupled Discharges of Molecular Gases*, G.F. Franz,*** Munich University of Applied Sciences, Germany

The heating of heavy plasma components by elastic collisions with electrons is one of the main mechanisms of energy transfer to ions and neutrals at low and medium power input, but often regarded inevitable. It is measured by optical emission spectroscopy, employing rovibrational bands of nitrogen, which is doped to capacitively coupled discharges of hydrogen and chlorine, and for comparison, also argon.@footnote 1,2@ The temperatures in chlorine are comparable to the inert gas argon, whereas hydrogen is significantly cooler, but all three will saturate at higher power inputs (more than 1/4 W/cm@super 2@ absorbed power density or at dc bias values higher than about 600 V). It is this region where parasitic processes (the most prominent is power absorption by ions in the sheath) will begin reducing the phase angle of power input from nearly perfect -90° to values of less than -20°. These data is discussed in terms of the functional dependence of electron density and electron temperature on discharge pressure and power input which have been recorded earlier.@footnote 3,4@ @FootnoteText@ @footnote 1@ M. J. Schabel, V.M. Donnelly, A. Kornblit, and W.W. Tai. Determination of Electron Temperature, Atomic Fluorine Concentration, and Gas Temperature in Inductively Fluorocarbon/Rare Gas Plasmas Using Optical Emission Spectroscopy, JVST A 20, 555 (2002)@footnote 2@ B. Bai and H.H. Sawin: Neutral Gas Temperature Measurements within Transformer Coupled Toroidal Argon Plasmas; JVST A 22, 2014 (2004)@footnote 3@ G. Franz: Comprehensive Analysis of Capacitively Coupled Chlorine-Containing Discharges, to be published in JVST A, May/June 2005@footnote 4@ G. Franz, M. Klick: Electron Heating in Capacitively Coupled Discharges and Reactive Gases, to be published in JVST A, 2005.

10:20am **PS-MoM7 Spatial and Temporal Measurement of Electric Fields in a Plasma*, E.V. Barnat,*** Sandia National Laboratories

We employ laser-induced dip-fluorescence to detect Stark shifts of atomic argon Rydberg states induced by electric fields present in the plasma sheath. The choice of the probed Rydberg state determines the electric field range and resolution we can achieve. Using the experimentally calibrated behavior of the Rydberg levels, both spatially and temporally resolved maps of the electric fields are obtained above powered electrodes generating a plasma. Electric fields around a technologiclly relevant electrode are mesured and compared to fields measured around simplified electrode structures. Both maps of the electric fields as well as excition and ionization profiels around the electrode demonstrates how the surfaces couple to the plasma. @FootnoteText@ This work was supported by the Division of Material Sciences, BES, Office of Science, U. S. Department of Energy and Sandia National Laboratories, a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

10:40am **PS-MoM8 Modified Actinometry for Monitoring Atomic Radicals in Molecular Gas Discharge*, T. Ishijima*,** *T. Okada, Y. Tanabe, H. Sugai,* Nagoya University, Japan

Actinometry technique has widely been used for detecting radicals in processing plasmas owing to its simplicity. There are many arguments on its reliability, especially from a viewpoint of electron-impact excitation processes. For example, one often encounters a serious difficulty in detecting atomic radical X in a discharge in diatomic molecule gas X@sub 2@: the dissociative excitation of X@sub 2@ induces the same optical emission line with the direct excitation of X, so that a standard actinometry taking the optical intensity ratio between actinometer (say, Ar) and the radical does not give the direct information of the radical density. Here we propose a method to discriminate a direct excitation component in the actinometry. This method is successfully applied to monitoring the N atom and the O atoms in high-density plasma nitridation and oxidation of silicon surface at low temperatures, respectively. The relative atomic densities obtained in the modified actinometry are compared with the absolute densities measured by appearance mass spectrometry. Preliminary measurements were applied in the the microwave excited plasmas of 2.45 GHz at 0.3 - 1.0 kW. The relative N atom densities are evaluated with N@super 4@P intensity (821 nm) normalized by Ar@super 2@P intensity (750 nm). When the pressure increases from 50 mTorr to 300 mTorr, both the absoulte N atom density and relative atomic densities increase monotonously in the same condition for input power and mixing ratio of Ar/N@sub 2@=9/1. Correlation with the measured atomic densities with the surface analysis data is discussed.

11:00am **PS-MoM9 Rare Gas and O Metastable Density in Rare Gas Diluted Oxygen RF Plasmas*, T. Kitajima,*** National Defense Academy of Japan, Japan*; K. Takahashi, T. Nakano,* National Defense Academy of Japan*; T. Makabe,* Keio University, Japan

Rare gas diluted O2 plasmas are interested for application to high quality SiO2 film formation. Especially, metastable O(1D) atoms produced in rare gas diluted O2 plasma is believed to promote higher production rate of the oxide films. The density of rare gas metastable atoms and O metastable atom in rare gas diluted O2 radio frequency (RF) capacitively coupled plasma (CCP) was measured by optical absorption spectroscopy (OAS). By decreasing O2 fraction in plasma, O(1D) metastable density icreases to twice of pure O2 plasma at 100 mTorr. Decreases of rare gas metastable densities due to addition of O2 indicate efficient O atom production by rare gas metastables via collisional quenching. Krypton metastable had highest density among four rare gas species for fixed RF power. The decrease of Ar metastable density due to O2 addition showed quantitative agreement with reported quenching rate coefficient. Detailed discussion on different gas pressures illustrates reduced O2 fraction is the key for selective production of O atoms through rare gas metastables.

11:20am **PS-MoM10 Prediction of Plasma UV Radiation Damages Using On-wafer Monitoring Sensors*, Y. Kato*,** *Y. Ishikawa, M. Okigawa, S. Samukawa,* Tohoku University, Japan

We have proposed a simple on-wafer monitoring sensor for prediction of UV and VUV photon radiation damages. In this sensor, the electrical currents were induced in the dielectric film and they could be measured by the plasma radiation. We first found that the current was completely corresponding to the generation density of hole-electron pairs in dielectric films and to the increase in interface state at the interface between the dielectric film and silicon under plasma irradiation. In this paper, the relationship between the induced electrical current in the sensor and plasma discharge conditions was investigated to predict the UV radiation damages. The dependence of the induced currents in the sensor on the plasma generation power, discharge pressure and gas flow rate was evaluated. Based on these results, we found that the UV radiation damages could be predicted and the low damage processes could be proposed for plasma etching processes.

11:40am **PS-MoM11 Sheaths and Pre-sheaths in Collisionless and Collisional Active Plasmas: Planar and Cylindrical Probes*, F. Iza,* *J.K. Lee,* Pohang University of Science and Technology (Postech), S. Korea

Ion kinetics in the sheath and pre-sheath of planar and cylindrical probes have been studied by means of particle-in-cell computer simulations. Low temperature argon discharges with Maxwellian electrons have been simulated in collisionless and collisional regimes. As pressure increases, the sheath, i.e. the region of positive space charge surrounding the probe, becomes collisional and the velocity of the ions entering the sheath falls below the Bohm velocity (u@sub B@). For planar probes, ions enter the sheath with a velocity given approximately by u@sub B@(1+4@lambda@@sub D@/@lambda@@sub i@) where @lambda@@sub i@ is the ion mean free path and @lambda@@sub D@ the Debye length at the sheath edge. This relation differs from that given in@footnote 1@ because the electric field boundary condition at the sheath edge used in@footnote 1@ corresponds to a field reached well inside the sheath. For a floating planar probe, the voltage drop across the sheath increases with pressure to balance the electron and ion fluxes and the ion flux is almost independent of pressure despite the variations in ion velocity. As observed experimentally,@footnote 2@ simulation results show that the voltage across the presheath can be significantly larger than half electron temperature. For planar probes, this voltage depends non-linearly on the electron temperature and increases rapidly for electron temperatures below 2eV. For cylindrical probes, however, the voltage across the presheath can be drastically reduced by the geometrical increase of current density as ions approach the probe. The floating potential and the ion velocity at the sheath edge decrease with decreasing probe radius and for thin probes (r@sub p@<@lambda@@sub D,i@), the voltage drop across the presheath is negligible (<<0.5T@sub e@). @FootnoteText@ @footnote 1@ V A Godyak and N Sternberg, IEEE Trans. Plasma Sci. 18 (1990) 159-168.@footnote 2@ L Oksuz and N Hershkowitz, Plasma Sources Sci. Technol. 14 (2005) 201-208.

Advanced Surface Engineering
Room 201 - Session SE-MoM

Nanocomposites and Coatings with Enhanced Thermal Stability

Moderator: J.M. Schneider, RWTH Aachen

8:20am **SE-MoM1 John Thornton Memorial Award Lecture: Understanding of the Preparation and Properties of Superhard Nanocomposites*, S. Veprek*[1]*,* Technical University Munich, Germany **INVITED**

Since the first report on the strong enhancement of hardness to 60-70 GPa in the Ti-Si-N system by Li Shizhi et al.,@footnote 1@ followed by the publication of the generic design concept,@footnote 2,3@ a large number of papers were published on this and similar systems which have led to some misunderstanding and controversies regarding the suitable deposition techniques and conditions, the maximum achievable value of hardness, the mechanism of the hardness enhancement, thermal stability and others. So far, plasma induced deposition techniques, such as glow discharge CVD, reactive sputtering and vacuum arc evaporation were used to prepare thin films of such materials. In my lecture I shall try to answer some of the open questions. First it will be shown how to differentiate between the superhard nanocomposites and coatings in which the hardness enhancement is due either to energetic ion bombardment during deposition or to solution hardening. The focus will be on the recent results regarding the spinodal nature of the phase segregation in this system, and on the thermodynamic and kinetic conditions needed to complete it during the deposition to obtain superhard nanocomposites with high thermal stability. The high hardness enhancement achieved in these materials is associated with the formation of a nanostructure where few nanometer small crystals of a hard transition metal nitride are "glued" together by about one monolayer of silicon nitride, as reported in our earlier HYPERLINK "mailto:work.@footnote"work.@footnote 1,2@ This finding was recently confirmed by the work of Oden et HYPERLINK "mailto:al.@footnote"al.@footnote 5@ on the preparation of high-quality heterostructures where the highest hardness enhancement was achieved for one monolayer of Si@sub 3@N@sub 4@. The first principle DFT calculations by C. Stampfl et HYPERLINK "mailto:al.@footnote"al.@footnote 6@ lend further support to this concept and show that, as predicted (see references quoted in@footnote 4@), such nanostructure reaches the ideal strength. The unusual combination of a high hardness, high resistance against crack formation and high elastic limit is a simple consequence of the almost flaw-free nature of these nanocomposites@footnote 4@ and of a finite activation volume for the initiation of plastic deformation within an amorphous HYPERLINK "mailto:phase.@footnote"phase.@footnote 7@) In order to correctly describe the mechanical properties of these materials, a new constitutive material's model was elaborated that accounts for the pressure enhancement of elastic moduli and of the flow stress. To be able to quantitatively describe the plastic deformation under conditions of a pressure dependent flow stress, the von Mises yield criterion had to be expressed in terms of a critical deviatoric strain. This model was then implemented into an advanced Finite Element Method code and the behavior of the materials upon indentation was studied in some HYPERLINK "mailto:detail.@footnote"detail.@footnote 8@ An important result of this work is the strong stiffening for both, elastic and plastic deformation due to the increase of the elastic moduli and of the flow stress by the high pressure under the indenter which is not found in conventional materials. The lecture will conclude with a brief overview of the recent industrial applications. @FootnoteText@ @footnote 1@ S. Z. Li, Y. Shi and H. Peng, Plasma Chem. Plasma Process. 12 (1992) 287. @footnote 2@ S. Veprek and S. Reiprich, Thin Solid Films 268 (1995) 64. @footnote 3@ S. Veprek, S. Reiprich and S. Z. Li, Appl. Phys. Lett. 66 (1995) 2640. @footnote 4@ S. Veprek, M. G. J. Veprek-Heijman, P. Karvankova and J. Prochazka, Invited Review, Thin Solid Films 476 (2005) 1. @footnote 5@ M. Oden, invited paper at the 51st Int. Symp. of the American Vacuum Society, Anaheim, November 14 – 19, 2004. @footnote 8@ S. Hao, B. Delley, and C. Stampfl, School of Physics, The University of Sydney, to be published. @footnote 7@ M. J. Demkowicz and A. S. Argon, Phys. Rev. Lett. 93 (2004) 025505-1. @footnote 8@ R. G. Veprek, D. M. Parks, A. S. Argon, and S. Veprek, to be published.

9:00am **SE-MoM3 Effect of Momentum Per Arriving Atom on nc-TiN/a-Si@sub x@N@sub y@ Nanocrystalline Composite Thin Film Properties in a Pulsed DC Magnetron Sputtering System*, P. Sunal,* *M.W. Horn,* The Pennsylvania State University

The mid-frequency pulsed dc range of 50-250 kHz was used to co-sputter nanocrystalline-TiN/a-Si@sub x@N@sub y@ films. A combinatorial process was performed in a reactive nitrogen environment from pure Ti and Si targets. An asymmetric bipolar pulsing frequency affects the plasma properties and results in a change in the density and energy of arriving ions at the growing film surface. The plasma potential, electron density, and electron temperature have been determined using a Langmuir probe and used with ion specie results from an energy resolved mass spectrometer to calculate the momentum per arriving atom. Using nanoindentation, the reduced modulus and hardness of the films were characterized and related to the plasma properties during deposition. The momentum per arriving atom shows threshold values for changes in the morphology, which result in different mechanical properties. Finally, the plasma properties were studied against the sputter pressure. At higher pulsing frequencies, the plasma potential increases causing energetic bombardment which yields smaller nanocrystal diameters and a stronger (200) preferred crystallographic orientation. Oxygen contamination of the thin films leads to degradation of the film properties and was investigated by using a silicon nitride capping layer to hermetically seal the film before leaving vacuum.

9:20am **SE-MoM4 Columnar Growth, Nanostructure and Properties of TiC/a-C:H Nano-Composite Coatings*, D. Galvan,* *Y.T. Pei, J.Th.M. De Hosson,* University of Groningen, The Netherlands

TiC/a-C:H coatings were deposited through closed field unbalanced magnetron sputtering (CFUBMS) reactive deposition. Different acetylene gas flow and substrate bias values were employed to vary the coatings composition and nanostructure. To improve adhesion between substrate and coating a Cr-Ti/Ti-TiC graded interlayer was introduced. Various techniques were employed to study the formation of TiC particles within the a-C:H matrix, e.g. EPMA, XPS, grazing angle XRD and high-resolution transmission electron microscopy (HR-TEM). The investigations provide detailed information about the TiC particles volume fraction, particle size and their size distribution in different coatings. It turns out that the Ti content affects to a great extent the columnar features. It is influenced by processing parameters such as deposition temperature or ion flux to atom flux ratio (ion number). An explanation of this effect is provided based on the observed nanostructure and the deposition technique employed. The mechanical performance of coatings with various chemical compositions was investigated through nano-indentations, focused ion beam (FIB) and

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[1] **John A. Thornton Memorial Award Winner**

TEM observations. It was found that the C-enriched columnar boundaries are the locations of crack nucleation and propagation. The investigations confirmed that a coating of low elastic modulus favors the redistribution of the applied load over a larger area, delaying the onset of plastic deformation and subsequent coating failure in these systems. The influence of the toughness of the coatings on their tribological performance is discussed.

9:40am **SE-MoM5 Smart Nanocomposite Tribological Coatings with Chameleon Behavior***, **A.A. Voevodin,*** Air Force Research Laboratory **INVITED**

A review of a recent progress in developing new tribological materials for operating across multiple environments relevant to aerospace applications is provided. New coating materials were designed to rearrange their structure and chemistry on demand to adapt to variable surface conditions (environment humidity, temperature). These materials have been dubbed chameleon because of their ability to change their surface chemistry and structure to avoid wear. The chameleon coating concept involves a nanocrystalline/amorphous nanocomposite structure, where individual phases are arranged to provide a high degree of mechanical and thermal stability and, at the same time, serve as nano reservoirs for tribological surface self-reconstruction. The stored materials are released from nanophase reservoirs in the process of wear and tribological surface chemistry and structure change to continuously reduce friction and wear. This surface response is triggered by changes in the operating environment and/or temperature. Several mechanisms are employed, including self-induced crystallization of amorphous dichalogenide phases, nucleation of nanograins of low melting point metals, formation of low melting point glassy ceramics, and change in the electron hybridization of carbon. These mechanisms were explored in sliding wear tests performed in controlled humidity air, dry nitrogen, and vacuum, as well as at high temperature in air.

10:20am **SE-MoM7 Optimization of Multilayer Wear-resistant Thin Films Using Finite Element Analysis***, **R.K. Lakkaraju**, F. Bobaru, S.L. Rohde,* University of Nebraska

Extensive research has been carried out by researchers on the growth and characterization of multilayer protective coatings, but the design of these coatings still remains largely empirical. In this regard, recent progress has been made in developing a design approach for optimizing multilayer coating structure before deposition which would help in saving time and material. In pursuit of optimal design, finite element analysis using a plane strain, hertzian contact model was developed to investigate the stress/strain behavior within the layers of the system. The present study looks to find optimal thicknesses of individual layers in the multi-layer coating-substrate system. First test case is a multiobjective optimization of a multilayer system performed by minimizing the strain discontinuities at the coating/substrate interface and the stresses developed in top layer, under combined normal and tangential load conditions. Another option is a single objective optimization (minimizing the strain discontinuity) by constraining the stress values below yield strength. We discuss the use and efficiency of optimization algorithms such as genetic algorithm and gradient based routines used in the present work, and the preliminary results are compared to pin-on-disk wear results of empirically designed coatings.

10:40am **SE-MoM8 Investigation on the Thermal Cycling Behaviour of Graded and Multilayered Lanthanum Zirconate as EB-PVD Thermal Barrier Coating***, K. Bobzin, E. Lugscheider, **N. Bagcivan,*** Surface Engineering Institute (IOT) RWTH Aachen, Germany

Thermal cycling behavior of thermal barrier coatings (TBC) is essential for the increase of efficiency of gas turbines. Traditionally Yttria partially stabilized Zirconia (YPSZ) coatings are used as TBCs on turbine blades. One approach within the collaborative research center (SFB) 561 "Thermally highly loaded, porous and cooled multilayer systems for combined cycle power plants" is to develop innovative TBCs to increase the overall efficiency of the power plant from 58% up to 65%. Investigations on some materials with perovskite, spinelle and pyrochlore structure have shown a great potential of Lanthanum Zirconate (pyrochlore) as thermal barrier coating. In this work Lanthanum Zirconate has been developed as TBC using electron beam physical vapour deposition (EB-PVD). TBCs deposited by EB-PVD show a columnar grain microstructure. A columnar grown TBC is able to balance the difference in thermal expansion between base material and TBC by the relative movement of the single columns. Two different coating architectures have been developed for the TBCs. First a multilayered TBC consisting of YPSZ and Lanthanum Zirconate has been deposited. In the second approach a graded TBC with a transition from YPSZ to Lanthanum Zirconate has been deposited by EB-PVD. The thermal cycling behavior of these coatings on Inconel Alloy 600 has been investigated by a thermal cycling test at 1050°C. Additionally the coatings have been characterized by x-ray diffraction (XRD), scanning-electron microscopy (SEM), energy dispersive X-ray analysis (EDX), and nanoindentation. The results of thermal cycling test show an increase of number of cycles before fatigue from 1380 cycles for YPSZ to 3390 cycles for graded YPSZ/Lanthanum Zirconate and 4140 cycles for multilayered YPSZ/Lanthanum Zirconate.

11:00am **SE-MoM9 Established Protective Cutting Tool Coatings for Difficult Machining Operations***, **K. Bobzin**, M. Maes, C. Pinero,* RWTH Aachen University, Germany **INVITED**

This paper presents a review of the most important thin coatings developed for the protection of cutting tools. Special attention was given to the development of promising coatings for difficult machining operations. Because of the increasing of the complexity in the aircraft and nuclear industry and the elevated operating temperatures, super alloys were developed from simple nickel-chromium matrix to multi-element, multi-phase systems. These new nickel-based super alloys are specially favored for their exceptional thermal resistance and ability to retain mechanical properties at elevated temperatures. However, they are classified as difficult-to-machine materials due to their high shear strength, work hardening tendency, highly abrasive carbide particles in the microstructures, strong tendency to weld and form built-up edges. Also, their tendency to maintain a high strength at the elevated temperatures generated during machining because of their low thermal conductivity constitutes an important challenge. Nowadays, TiAlN is well known because of its excellent overall performance in cutting operations. Also crystalline Al@sub 2@O@sub 3@ shows a high potential for the protection of cutting tools due to its very good chemical and thermal properties. However an adequate coating system for machining super alloys was not found yet. In order to obtain the appropriated properties combination in a single coating system, different TiAlN + @gamma@-Al@sub 2@O@sub 3@ coating system combinations were deposited on cemented carbide cutting inserts and characterized by X-ray diffractometry (XRD) and scanning electron microscopy (SEM). Surface energy of the coated samples was measured. Tribological and chemical properties were analyzed at room and high temperatures.

11:40am **SE-MoM11 Multifunctional SiAlON Ceramic Coatings for High Temperature Applications***, J.I. Krassikoff, D.J. Frankel, T.A. Dunn, D.R. Southworth, **R.J. Lad,*** University of Maine

SiAlON ceramics possess oxidation resistance, high strength, and thermal shock resistance, which make them extremely attractive for applications in 1000-1500°C oxidation environments. We have investigated well-defined SiAlON thin films deposited by rf magnetron co-sputtering of Al and Si targets in Ar/O@sub 2@/N@sub 2@ mixtures. By precisely controlling film architecture at the nanometer level, coating structures having homogenous, gradient, or multilayer compositions that span the full range of O/N and Al/Si ratios have been synthesized, and their chemical, thermal, and mechanical properties have been characterized. Nitride-rich SiAlON film compositions are extremely wear resistant, yet they become oxidized during thermal treatments in air between 1000-1500°C. Compositionally graded coatings with oxide-rich terminations show improved oxidation resistance. Similarly, Al@sub 2@O@sub 3@/Si@sub 3@N@sub 4@ laminate structures exhibit low wear and chemical stability at high temperature. Photolithographically patterned thin film metal resistors embedded at the SiAlON/substrate interface have been used to quantify the oxygen penetration rates through the SiAlON film structures during isothermal annealing and thermal cycling experiments. Accelerated testing consisting of rapid thermal cycling in various reactive environments was accomplished using a microfabricated heater platform. The role of film stress on resulting mechanical properties was investigated using microfabricated cantilever structures.

Surface Science
Room 202 - Session SS1-MoM
Catalytic Chemistry of Hydrocarbons

Moderator: M. Trenary, University of Illinois at Chicago

8:20am **SS1-MoM1 Transition States of Hydrogenation and @beta@-hydride Elimination in Alkyl Groups on the Pt(111) Surface***, P.P. Ye, A.J. Gellman,* Carnegie Mellon University

Substituent effects have been used to probe the characteristics of the transition states to hydrogenation of alkyl groups and the transition state to @beta@-hydride elimination in alkyl groups on the Pt(111) surface. Eight different alkyl and fluoroalkyl groups have been formed on the Pt(111) surface by dissociative adsorption of their respective alkyl and fluoroalkyl iodides. Co-adsorption of hydrogen and subsequent heating of the surface results in hydrogenation of the alkyl groups to alkanes which desorb into the gas phase. The influence of the substituents on the activation barriers to hydrogenation has been correlated to the field and polarizibility substituent constants of the alkyl groups in the form of a linear free energy relationship. Increasing both the field and polarizibility constants of the alkyl groups increases the barrier to reaction. These substituent effects indicate that the a-carbon in the transition state is cationic with respect to the initial state of alkyl group and that the reactant has greater charge density on the a-carbon than the transition state. In the absence of adsorbed hydrogen, alkyl groups on Pt(111) dehydrogenate via @beta@-hydride elimination. In the fluorinated alkyl groups this then leads to the deposition of hydrogen on the surface and the hydrogenation of the intact fluoroalkyl groups to form fluoroalkanes. The desorption kinetics of the product fluoroalkanes serves as a measure the kinetics of the @beta@-hydride elimination. The field effects of the fluorinated substituents increase the barriers to @beta@-hydride elimination. The interpretation of this effect is that the @beta@-carbon atom in the transition state is cationic with respect to the reactant. This is consistent with observations made on the Cu(111) surfaces although the substituent effect is smaller on the Pt(111) surface indicating a difference in the nature of the transition states on the two surfaces.

8:40am **SS1-MoM2 Surface Science Insights on the Enantioselective Hydrogenation of Activated Ketones on Chirally-Modified Platinum***, S. Lavoie, P.H. McBreen,* Université Laval, Canada

The asymmetric hydrogenation of alpha-ketoesters on chirally-modified platinum catalysts, the Orito reaction, involves a complex set of interrelated interactions. These include the chemisorption of the chiral modifier and the ketoester on the metal surface, as well as the modifier-ketoester interactions responsible for enantiodifferentiation. In order to isolate the key modifier-ketoester interactions, RAIRS studies were performed on a range of aromatic-carbonyl co-adsorption systems of progressively increasing complexity. All effective modifiers for the Orito reaction contain both an extended aromatic function and a function capable of conventional H-bonding. It is generally accepted that the aromatic function serves to anchor the chiral modifier to the platinum surface, and that it may also play a steric role in inducing asymmetry. However, evidence will be presented for a key additional role for the aromatic anchor. Using results for the Pt(111) surface, it will be shown that the modifier-ketoester interaction may be described in terms of two distinct H-bonds, one of which is to the chemisorption activated aromatic system. It will be shown that such a two-point H-bonding interaction can account for most observations in the catalysis literature concerning the Orito reaction.

9:00am **SS1-MoM3 Electronic States of Adsorbed Molecules and Vibrational Excitation by Inelastically Tunneled Electrons from STM Tip***, M. Kawai,* RIKEN and University of Tokyo, Japan **INVITED**

The inelastic tunneling process of electrons between the tip of an STM and the target molecule can lead to various dynamical processes at surfaces such as desorption, lateral hopping, rotation and chemical reaction via the excitation of vibrational modes of adsorbed molecules. The vibrational mode that are excited through the process could be defined through the response of the molecular motion to the applied bias voltage, i.e. action spectrum. Action spectra for hopping motion of cis-2-butene on Pd(110), cleavage of dimethl-disulfide on Cu(111) and hopping motion of cleaved product methyl-thiol show clear thresholds in bias voltage that are equivalent to certain vibration modes, the excitation mechanism of which can be understood by the resonant tunneling mechanism. When the electron jumps into or out of a certain molecular orbital, molecules will temporally go through the negative or positive ion state. And vibration states can be excited, during the relaxation process. Inelastic process that leads to vibrational excitation has attracted much attention of since the conductivity of molecules bridging the electrodes is found to be strongly affected when they are vibrationally excited. Considering that the conduction electrons passes through the electronic state crossing the Fermi level or hopping through the HOMO or LUMO state of the molecule, the electronic state of adsorbate should play a crucial role in the molecular electronics as well as the chemical reactions at surfaces.

9:40am **SS1-MoM5 The Reaction Pathway for the Synthesis of Vinyl Acetate on Pd(111)***, W.T. Tysoe, F. Calaza, D. Stacchiola,* UW-Milwaukee

The palladium-catalyzed synthesis of vinyl acetate from acetic acid, ethylene and oxygen is studied on Pd(111) single crystal surfaces. The rate of reaction between gas-phase ethylene and adsorbed acetate species is followed using infrared spectroscopy by measuring the time dependence of the intense OCO acetate mode at 1414 cm@super -1@. The acetate removal kinetics are modeled by assuming that ethylene adsorption is blocked by acetate species. Temperature-programmed reaction confirms that vinyl acetate is formed in the reaction. The reaction pathway is explored by comparing the reaction rates of d-@sub 4@-, 1,1-d@sub 2@-, 1,2-d@sub 2@ and normal ethylene with surface acetates. d@sub 4@-ethylene reacts about six times more slowly than C@sub 2@H@sub 4@ indicating that hydrogen is involved in the rate-limiting step. The reaction rates are different for 1,1-C@sub 2@H@sub 2@D@sub 2@ and 1,2-C@sub 2@H@sub 2@D@sub 2@. This indicates that vinyl acetate formation occurs via the insertion ethylene into the surface acetate species to form an acetoxyethyl-palladium intermediate, which then reacts to form vinyl acetate via a @beta@-hydride elimination reaction, rather than by vinyl formation and addition to the acetate species to form vinyl acetate. The different reactivities of the isotopomers is rationalized by making the reasonable assumption that ethylene adsorption is blocked by the acetoxyethyl-palladium intermediate. When reaction is carried out using 1,1-C@sub 2@H@sub 2@D@sub 2@, the intermediate can be formed with exclusively deuterium atoms in the @beta@-position, slowing its rate of decomposition, blocking ethylene adsorption, and slowing the reaction rate. Reaction with 1,2-C@sub 2@H@sub 2@D@sub 2@ results in one hydrogen being in the @beta@-position, allowing it to decompose more rapidly. Final conformation of this pathway comes from detecting the acetoxyethyl-palladium intermediate using infrared spectroscopy when reaction is carried out using C@sub 2@D@sub 4@.

10:00am **SS1-MoM6 Vinyl Acetate Synthesis on Pd-based Catalysts: Structure Sensitivity and Active Site Identification***, D. Kumar, M.S. Chen, Y.F. Han, C.-W. Yi, K. Luo, D.W. Goodman,* Texas A&M University

The synthesis of vinyl acetate (VA) is a very important industrial reaction and is produced by acetoxylation of ethylene over Pd-Au catalysts. Historically this highly selective reaction has been studied using conventional kinetic techniques; however, there is no consensus regarding a reaction mechanism. A combination of surface science techniques and kinetic measurements has been used in the current study to address the structure sensitivity and the active ensemble for the reaction. VA synthesis was carried out over Pd and Pd-Au high-surface-area and model planar catalysts and the reaction rates found to be: Pd(100) < 5 wt% Pd/SiO2(d@sub Pd@=4.0nm) < 1 wt% Pd/SiO2(d@sub Pd@=2.5nm). A particle size dependence of the reaction rates implies a degree of structure sensitivity. Furthermore, the addition of Au to Pd/SiO2 catalysts leads to a significant increase in the reaction rate and selectivity with the latter related directly to a change in the reaction order with respect to ethylene. Infrared reflection absorption spectroscopy (IRAS) of CO on Pd/Au(100) and Pd/Au(111) confirms that Pd is present as isolated monomers on a Au-rich surface. A pair of Pd monomers is the optimum active site for the adsorption of ethylene and acetate species, and leads to the formation of VA. The spacing between the two active Pd monomer pairs is crucial on Au(100) and Au(111), evident by the relative rates of VA synthesis on Pd/Au model catalysts, i.e. Pd/Au(111) < Pd/Au(100).

10:20am **SS1-MoM7 Selective Oxidation of Hydrocarbons on Chemisorbed Oxygen Covered Au(111)***, X. Deng*[1]*, C.M. Friend,* Harvard University

Chemisorbed oxygen covered Au(111) has been found to be active for the partial oxidation of hydrocarbons. Specifically, chemisorbed oxygen on a herringbone-Au(111) was deposited via electron-induced dissociation of NO2. Several hydrocarbons, including cyclohexene and styrene, were studied on the O/Au surface by using temperature programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS). The

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[1] **Morton S. Traum Award Finalist**

primary products are styrene epoxide and benzene for styrene and cyclohexene oxidation, respectively. HREELS was performed to identify the intermediates of the reactions. In combination with the observed isotope effects, the reaction mechanisms on O/Au(111) were proposed and compared with those on O/Ag(110).

10:40am **SS1-MoM8 Reactivity Studies of Molybdenum Carbide Nanoparticles formed on Au(111) using Reactive-Layer Assisted Deposition***, **D.V. Potapenko**,* BNL*; J.M. Horn, M.G. White,* BNL and SUNY at Stony Brook

The chemical properties of MoC@sub x@ nanoparticles prepared by a novel method on the Au(111) support have been studied using cyclohexene, cyclohexane and benzene as test molecules. The surfaces have been prepared by depositing Mo by physical vapor deposition (PVD) on a reactive layer of ethylene, which was physisorbed on a Au(111) substrate at low temperatures (85 K). STM imaging shows that the resulting MoC@sub x@ particles have a narrow size distribution and preferentially nucleate near the 'elbow' sites on the reconstructed (22 x @sr@3)-Au(111) surface. Auger and XPS indicate that the MoC@sub x@ particles are near stoichiometric (x = 1). Also we have found that in the thermodynamically stable state MoC@sub x@ particles are partially encapsulated by gold from the support. Thermal programmed desorption (TPD) studies have shown that cyclohexene undergoes three different reactions on bare (not encapsulated by Au) MoC@sub x@ nanoparticles: hydrogenation to cyclohexane, partial dehydrogenation with benzene formation, and complete dehydrogenation with surface carbon deposition. In contract, interaction of cyclohexene with Au-encapsulated MoC@sub x@ nanoparticles exhibits a very high (at least 95 %) selectivity toward partial dehydrogenation to benzene. The found selectivity is higher than that for cyclohexene reactions on either C/Mo(110) or Pt(111) surfaces. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences under contract No. DE-AC02-98CH10886.

11:00am **SS1-MoM9 The Mechanism of Partial Oxidation of Styrene on Ag(111)***, **A. Klust**, R.J. Madix,* Stanford University

The partial oxidation of olefins on Ag surfaces has been a long standing problem in surface science and is of great commercial interest. In particular, the nature of reaction intermediates has been subject of intense debate. One candidate for the reaction intermediate is the oxametallacycle where both ends of a -C-C-O- chain are attached to the Ag surface (see e.g. [1]). We present a temperature programmed reaction spectroscopy (TPRS) and x-ray photoelectron spectroscopy (XPS) study of the partial oxidation of styrene on Ag(111). The reaction products are CO@sub 2@, H@sub 2@O, styrene oxide, benzene, and benzoic acid. XPS gives evidence for two different intermediate structures that we assign to an oxametallacycle and to benzoate. The oxametallacycle seems to be the precursor for the formation of the styrene oxide as well as for the formation of the benzoate while the benzoate itself leads to the formation of CO@sub 2@, benzene, and benzoic acid. The results are explained in the framework of a model based on the asymmetry of the oxametallacycle caused by the phenyl ring of styrene. @FootnoteText@ @footnote 1@ S. Linic and M. A. Barteau, J. Am. Chem. Soc. 125 (2003) 4034.

11:40am **SS1-MoM11 Catalytic Hydrodechlorination of Chlorobenzene and Chlorotoluene Isomers on the Pt(111) Surface***, **B.M. Haines**,* University of Michigan*; D.A. Fischer,* National Institute of Standards and Technology*; J.L. Gland,* University of Michigan

The catalytic hydrodechlorination of chlorobenzene on the Pt(111) surface has been characterized using temperature programmed reaction spectroscopy (TPRS) and fluorescence yield near edge spectroscopy (FYNES) above the carbon K edge. Thermal hydrodechlorination, dehydrogenation and rehydrogenation result in the formation of benzene, HCl, and H@sub 2@ when chlorobenzene is heated on platinum. The effects of methyl substituents on hydrodechlorination were probed using the isomers of chlorotoluene. The chlorobenzene monolayer adsorbs on the Pt(111) surface with the plane of the ring at a 45° angle from the surface as indicated by FYNES. The monolayer partially desorbs at 196 K and the remaining chlorobenzene then undergoes dechlorination via two reaction channels at 270 K and at 420 K as shown by TPRS. Comparison of the integrated peak areas for these two channels yields a 3:2 (270 K: 420 K) ratio. Temperature programmed-FYNES show that a stable cyclohexadiene intermediate is formed above 250 K that is coadsorbed in a 3:2 ratio with molecular chlorobenzene. The remaining molecular chlorobenzene is dechlorinated in the 420 K range to form additional adsorbed cyclohexadiene. For chlorotoluene, substituent effects dominate activation of the C-Cl bond through the ring and dehydrogenation of the methyl group at low temperatures.

Surface Science
Room 203 - Session SS2-MoM

Oxide Surface Structure and Characterization

Moderator: M.A. Henderson, Pacific Northwest National Laboratory

8:40am **SS2-MoM2 Thermodynamic Stability of Alumina Films on NiAl(110) and the Dynamics of Their Extended Defects***, **K.F. McCarty**, N.C. Bartelt, J.P. Pierce,* Sandia National Laboratories*; C.B. Carter,* University of Minnesota

A well-studied oxide surface is the thin-film alumina formed by oxidizing a NiAl(110) surface [J. Libuda et al., Surf. Sci. 318 (1994) 61]. Here, we show how low-energy electron microscopy (LEEM) can determine the thermodynamic stability of these alumina films and image the formation and time evolution of extended crystallographic defects. At sufficiently high temperature, discrete islands of crystalline oxide form when NiAl is exposed to oxygen. Analysis by electron diffraction and scanning tunneling microscopy establish that these oxide islands are the same alumina produced by the literature "recipe." We directly measure the thermodynamic stability (Gibbs formation energy) of the alumina -- at a fixed temperature, the pressure of oxygen in equilibrium with the oxide is determined by finding the pressure at which individual alumina islands neither shrink nor grow. We find that the equilibrium oxygen pressure of the thin-film alumina is many orders of magnitude greater than bulk alumina. Analysis suggests that strain is the cause of the remarkable instability of the alumina film. We also investigate how two types of planar defects in the films, boundaries between rotational and translation domains, originate and evolve. Typically, domains in films are thought to originate from the nucleation stage of film growth. That is, domain boundaries occur where rotated or translated islands impinge. Indeed, we observe that rotational boundaries form in this manner. In contrast, translation ("antiphase") boundaries are observed to nucleate, grow, and even move within isolated oxide islands. The fact that translation boundaries form within isolated alumina islands strongly suggests that the boundaries are introduced to relieve strain. We will discuss how formation of translation domains reduces film strain. This work was supported by the Office of Basic Energy Sciences, Division of Materials Sciences of the U.S. DOE under Contract No. DE-AC04-94AL85000.

9:00am **SS2-MoM3 Growth and Properties of Vanadia on Anatase TiO@sub 2@ (001) and (101) Surfaces***, **W. Gao**,* Yale University*; R. Klie,* Brookhaven National Laboratory*; E.I. Altman,* Yale University

Inspired by its unique catalytic properties and elusive structure, we have been studying the structure of vanadia layers deposited onto epitaxial anatase (001) and (101) films. For anatase (001), a (1x4)/(4x1) reconstruction was observed by reflection high-energy electron diffraction (RHEED) and low energy electron diffraction (LEED). After depositing 1 ML at 525 K, X-ray photoelectron spectroscopy (XPS) showed predominantly V@super 5+@ and the (1x4)/(4x1) diffraction patterns were replaced by (1x1) patterns indicating that vanadia lifts the reconstruction and the monolayer is pseudomorphic. Continued growth caused the RHEED pattern to fade, suggesting that V@sub 2@O@sub 5@ epitaxy cannot be continued beyond 1 ML. At 750 K, however, VO@sub 2@ formed and the (1x1) pattern remained clear for 20 nm of vanadia. At 800 K, a c(2x2) termination was observed. These results suggest that the V@super 5+@ in the monolayer is due to 0.5 ML of terminal oxygen which allows epitaxy and the 5+ oxidation state. These results were compared with those for anatase (101) surfaces, the lowest energy anatase surface. The (101) surfaces were formed by depositing TiO@sub 2@ onto LaAlO@sub 3@(110). Although x-ray diffraction and scanning transmission electron microscopy indicated that the films grew with anatase (102) planes parallel to the interface, RHEED and LEED showed the surface diffraction patterns expected for a (101) surface and STM showed the oblique unit cell of the (101) surface. These conflicting results were attributed to the surface faceting to expose the lowest energy (101) surface. Similar to anatase (001), a (1x1) diffraction pattern is maintained after depositing 1 ML of V@sub 2@O@sub 5@; however, further vanadia deposition led to three dimensional vanadia clusters. STM is being used to further characterize the structure of the vanadia monolayers on the two anatase surfaces.

9:20am **SS2-MoM4 Oxide Nanolayers: Artificial Phases in Low Dimensions***, **F.P. Netzer**, S. Surnev, J. Schoiswohl, G. Parteder, M.G. Ramsey,* Karl-Franzens-University Graz, Austria*; G. Kresse,* University of Vienna, Austria

Transition metal oxides in ultrathin nanostructured layers on well-defined metal surfaces may form novel oxide phases, that do not occur in nature. These "artificial oxide phases" display new physical and chemical properties, which make them potentially interesting materials for nanotechnology applications. They derive their formation, on the one hand, from the interactions at the interface between the oxide overlayer and the metal substrate and, on the other hand, from kinetic constraints during the growth process. The growth of a variety of novel low-dimensional vanadium, nickel, and manganese oxide structures on Rh and Pd single crystal surfaces has been followed and the surface phase diagrams and the atomic structures of oxide nanolayer phases have been characterised by the interplay of various experimental and theoretical methods (STM, LEED, UPS and XPS, HREELS, ab initio DFT). The influence of energetic and strain effects at the interface is important and determines the particular structures, which are observed on different substrates. The oxide structures to be discussed comprise highly oxidised (nominally V@sub3@O@sub9@), mixed valent (VO@sub1.6-2.09@), and reduced (nominally V@sub2@O@sub3@) vanadium oxide surface phases on Rh(111) and Pd(111) substrates, a c(4x2) wetting layer of an interfacial nickel oxide on Pd(100), which acts as an interlayer to cubic NiO growth, and various manganese oxide phases on Pd(100). It is shown that, in addition to the thickness confinement in the nanolayers, the lateral confinement as imposed by the regular step array on a vicinal substrate surface can promote the growth of novel oxide nanostructures. @FootnoteText@ Supported by the Austrian Science Fonds and the EU STREP Programme GSOMEN.

9:40am **SS2-MoM5 Metal Atoms and Clusters on Oxide Surfaces and Thin Films: Charging Mechanisms and Consequences***, **G. Pacchioni**,* Universita' di Milano-Bicocca, Italy **INVITED**

Metal clusters deposited on oxide surfaces exhibit specific chemical and physical properties often connected to their low dimensionality. The properties of truly nano-clusters a few atoms in size or even of isolated metal atoms are highly depending on the type of oxide support, adsorption site, surface morphology, etc. One of the aspects that can deeply modify the properties of the adsorbed metal atoms or clusters is the occurrence of charge transfers at the metal-oxide interface. Recent studies have shown that charged clusters, and in particular cluster anions, are catalytically more active than their neutral counterparts. Charging mechanisms of metal atoms and clusters on oxide surfaces is the topic of this talk. Using high quality electronic structure calculations in combination with experimental spectroscopic measurements, we will discuss in which conditions charging occurs and how to measure it. The systems considered are metal atoms like Cu, Au, Pd, on oxide substrates like MgO, SiO2, and TiO2 single crystals or in polycrystalline or amorphous form. We will show that a major role in charging of the deposited atoms is played by point defects at the oxide surface and discuss methods to prove the occurrence of the charge transfer. In the second part of the talk we will examine methods to induce charging even without implying the presence of defects. In particular, we will consider metal atoms deposited on ultra-thin oxide films epitaxially grown on metal single crystals. We will discuss the adsorption properties of Pd, Ag, and Au atoms on 1 to 5 layers thick films of MgO on Mo(100) and compare them to those of MgO(100) single crystals. On supported MgO thin films charging can occur from the metal substrate to adsorbed atoms with high electron affinities, like Au. We will discuss possible mechanisms for this charge transfer like direct tunneling or dielectric breakdown induced by an external electric field.

10:20am **SS2-MoM7 Growth of WO@sub 3@ Clusters on TiO@sub 2@(110)-(1x1).***, **O.A. Bondarchuk**,* University of Texas at Austin*; Z. Dohnalek, B.D. Kay, J. Kim,* Pacific Northwest National Laboratory*; J.M. White,* University of Texas at Austin

Tungsten oxide clusters supported on Al@sub 2@O@sub 3@, SiO@sub 2@, ZrO@sub 2@ and TiO@sub 2@ are known to be catalytically active for a wide range of acid-catalyzed reactions including alcohol dehydrogenation, alkane hydrogenation, metathesis etc. In this work, we studied the growth of WO@sub 3@ nanoclusters on TiO@sub 2@(110)-(1x1) surface using STM. Submonolayer amounts of WO@sub 3@ were deposited on TiO@sub 2@(110) via direct, thermal evaporation from WO@sub 3@. Using XPS we have determined that WO@sub 3@ deposited on TiO@sub 2@(110) is thermally stable and remains fully oxidized up to 700 K. Atomically resolved studies of WO@sub 3@ deposited at room temperature on TiO@sub 2@(110) show only fuzzy, poorly defined features indicating that the clusters are only weakly bound to the substrate. Subsequent annealing to 600 K results in the formation of bright (WO@sub 3@)@sub x@ clusters that can be easily imaged. In case of low WO@sub 3@ coverages (< 0.25 ML) the STM images indicate that the majority of clusters have identical size (~0.6nm in apparent diameter) and position with respect to the substrate registry. The amount of deposited WO@sub 3@ from a quartz crystal microbalance measurement together with the observed cluster density yields the upper bound of x @<=@ 3 for the number of W atoms in each cluster. Additionally, annealed (WO@sub 3@)@sub x@ clusters exhibit preferential alignment across the Ti4+ rows suggesting attractive interactions between them.

10:40am **SS2-MoM8 Imaging of Atoms on Oxide Surfaces by X-ray Standing Wave Fourier Inversion***, **C.-Y. Kim**,* Northwestern University*; J.W. Elam,* Argonne National Laboratory*; D. Goswami, M.J. Bedzyk, P.C. Stair, S Christensen, M.C. Hersam,* Northwestern University

Supported metal oxides are among the most important of catalytic materials systems. However, there is a lack of experimental atomic-scale structural information for describing the relevant interfaces. We combine atomic layer deposition (ALD) and x-ray standing wave (XSW) atomic-imaging to address this challenge. As a first case, we determine the precise registry of W atoms on a rutile TiO2(110) surface. XSW results show that tungsten has an average adsorption height of 3.48 @Ao@. above the Ti-O plane. The direct-space image reveals that W occupies the Ti-site that would be occupied by Ti if the bulk structure were extended above surface. The tungsten atoms are vertically shifted upward from the ideal Ti-site location by +0.23 @Ao@. We speculate that the sacrificial role of Si2H6 in removing surface species may apply to the TiO2 substrate in addition to the W ALD film. This is the first atomic structure determination of a supported catalytic phase under ambient conditions. The results suggest that supported metal cations locate as if they were the next layer in the bulk structure. The ALD method for supported catalyst material preparation provides a bridge over the "materials preparation gap" that typically separates practical, high-surface-area and single crystal model catalytic materials.

11:00am **SS2-MoM9 Terminal Oxygen Structures on WO@sub 3@(100) Thin Films***, M. Li, A. Posadas, C. Ahn, **E.I. Altman**,* Yale University

Scanning tunneling microscopy (STM) was used to characterize the surface reconstructions on epitaxial WO@sub 3@(100) thin films on LaAlO@sub 3@(100) in a reducing environment. As the films were annealed between 600-770 K, a myriad of surface structures related to terminal oxygen were observed. Upon initial reduction the surface was covered with small c(2x2), p(2x2), c(4x2), and poorly ordered terminal oxygen terraces all coexisting with (1x1) islands. Further reduction caused large flat terraces of poorly ordered terminal oxygen to coexist with strand terminated p(nx2) terraces with n = 3-5. Continued reduction led to a zigzag arrangement on top of the p(nx2) surface, half-height p(2x2) and c(4x2) islands, and a local (15x2) structure. The latter three structures could only be explained by crystallographic shearing of the surface plane. In contrast to higher annealing temperatures, the exclusively p(nx2) terminated surface characterized by alternating strands and troughs was not observed, suggesting that at lower temperatures crystallographic shear competes with the bulk migration responsible for trough formation as the dominant surface reduction mechanism.

Thin Films
Room 306 - Session TF+EM-MoM
Thin Films for Photovoltaic and Energy Applications

Moderator: B.C. Holloway, College of William and Mary

8:20am **TF+EM-MoM1 Hydrogen - The World of Tomorrow?***, **G.N. Richter**,* Chevron Fellow Emeritus **INVITED**

We have all heard of the coming world of hydrogen, and how it will become our energy carrier of choice, both clean and efficient, a major input for many chemical processes and, perhaps, our saviour. I am sure that this is coming, and it will bring a major change to many things we do. It will take a revolution to bring this about and it won't be until some time in the future. The question isn't if it will happen, but when will it come and what is needed to bring it about? Others at this meeting are telling us of the uses of hydrogen, its promises and its behaviour. But, there are also important questions to ask about where will the hydrogen come from and the infrastructure needed for us to be able to use it. It is the difficulty in answering these questions that is holding back the revolution. And it is these points that I would like to discuss with you today. Not the promises we have all heard, but how we can get to this "promised" land, as well as some of the things we might all do to get there sooner. What are the needs and opportunities for all of us to address?

9:00am **TF+EM-MoM3 Carbon Nanotube Catalyst for PEM Fuel Cells***, **J. Narayanamoorthy**, S. Durairaj, J. Choi,* Wayne State University

Carbon nanotubes have unique properties for future fuel cell applications such as diverse electrical properties, large surface area to volume ratio, chemical inertness, etc. The role of carbon nanotubes for the polymer electrolyte fuel cell has been investigated. First, the morphological, electrical, and mechanical role of the carbon nanotubes in the catalyst layer was studied. There was minimal cracking and maximal interconnect in the layer with carbon nanotubes. The resistance of the catalyst layer reduced due to the presence of carbon nanotubes and mechanical properties also showed good improvement. Further, carbon nanotubes themselves were employed as catalyst in place of noble metals and were optimized by tuning the electronic properties of carbon nanotubes. In this presentation, we will discuss the correlation between catalytic activity and the electronic structure of carbon nanotubes.

9:20am **TF+EM-MoM4 Growth of CIGSS Thin Film Solar Cells on Flexible Stainless Steel Substrates of Various Thicknesses***, **A. Kadam**, A. Jahagirdar, N.G. Dhere,* University of Central Florida

The article presents the effect of surface roughness and thicknesses of stainless steel(SS) substrates on the growth behavior of CuIn@sub 1-x@Ga@sub x@Se@sub 2-y@S@sub y@(CIGSS) absorber thin film solar cells. The work was carried out on 430 grade SS of thicknesses 25 µm, 50 µm and 127 µm. Surface roughness gradually decreased from 254 Å for 25 µm to 62.3 Å for 127 µm substrate. Thinner foil has higher surface roughness as it required more processing steps. Deposition sequence was Mo/SS/Mo/CIGSS/CdS/i:ZnO/ZnO:Al/Ni/Al. Mo back contact and Cu-Ga-In metallic precursors were deposited by DC magnetron sputtering. Mo was deposited on both the sides of SS to prevent the reaction of selenide and sulfide gases with SS during processing. Mo was deposited in a three-layer sequence. Mo layer deposited at low DC power and high argon gas pressure develops tensile stress while that deposited at high power and low pressure exhibits compressive stress. Tensile layer was sandwiched between two compressive layers to reduce the overall stress and to build the thickness of 500 nm. Identical parameters were used for deposition of metallic precursors on all three substrates. The elemental stack was selenized at 400@super o@C for 10 minutes followed by sulfurization at 475@super o@C for 20 minutes. CdS, n-type hetero-junction partner was deposited by chemical bath deposition. Window bilayer of i:ZnO and ZnO:Al were deposited by RF magnetron sputtering and Ni/Al contact fingers were deposited by e-beam evaporation. The crystal structure, surface morphology, chemical variation and cell efficiency were studied using the characterization technique such as x-ray diffraction, scanning electron microscopy, Auger electron spectroscopy, transmission electron microscopy, current-voltage and quantum efficiency measurement to bring out the variation in the growth behavior and cell efficiency on substrates having varied physical properties.

9:40am **TF+EM-MoM5 Surfactant-assisted Growth of CdS Thin Films for Photovoltaic Applications***, **C.L. Perkins**, F.S. Hasoon,* National Renewable Energy Laboratory

A common non-ionic surfactant, Triton X-100, was used to modify the chemical bath deposition (CBD) of CdS "buffer" layers on Cu(In,Ga)Se@sub 2@ (CIGS) thin films. X-ray photoelectron spectroscopy and Auger electron spectroscopy data demonstrate that films produced with the surfactant have about the same levels of impurities as films grown without it. It was found that Triton X-100 allowed the use of CdS layers that were 3-4 times thinner than those used normally in high efficiency CIGS-based devices, with no loss in cell performance. For these thin CdS layers and relative to devices made without the surfactant, average absolute cell efficiencies were increased from 10.5% to 14.8%, or by a relative 41%. Visual inspection of the CdS depositions reveals one possible mechanism of the surfactant's effects: bubbles that form and adhere to the CIGS surface during the chemical bath deposition are almost completely eliminated with the addition of the TX-100. Thus, pinholes and thin areas in the CdS layers caused by poor wetting of the substrate surface are sharply reduced, leading to large increases in the open circuit voltage in devices produced with the surfactant.

10:00am **TF+EM-MoM6 Surface Energies and Surface and Grain Boundary Nanochemistry of Cu(In,Ga)Se@sub 2@***, C. Lei, D. Liao, A. Hall, I.M. Robertson, **A. Rockett**,* University of Illinois

A combination of angle-resolved photoelectron spectroscopy, atomic force microscopy, and analytical high-resolution transmission electron microscopy including nanoprobe energy dispersive spectroscopy (EDS) and angular darkfield imaging have been used to characterize the surfaces and grain boundaries in a wide variety of Cu(In,Ga)Se@sub 2@ epitaxial single crystal and polycrystalline thin films. We have observed the formation of a wide variety of nanoscale and microscale voids in polycrystalline grain boundaries and in heteroepitaxial interfaces. It is argued that these are Kirkendall voids. Likewise, trapped internal voids within grains are observed in dislocation cores and at twin termination boundaries. These have been analyzed and a Wulff construction developed to characterize the surface energies in the material. The results show that the polar metal-terminated (112) planes are the lowest energy surfaces, followed by the Se-terminated (112) planes. These results are consistent with the surface morphology of growing epitaxial layers of various orientations, indicating that the surface faceting is a largely equilibrium rather than kinetically-determined result. Other planes are stable when covered by a surfactant layer of Cu@sub 2@Se, which occurs naturally when the film is deposited in an average Cu-rich condition. Grain boundaries are also found to exhibit faceted growth. Surprisingly, in spite of these surfaces being polar, no chemistry change is observed with nanoprobe EDS in the grain boundaries relative to the bulk grains for films grown at high temperatures. For low temperature depositions (below 450°C), non-equilibrium grain boundary compositions are observed. Clean metal-terminated (112) surfaces are shown to have Fermi energies higher in the energy gap when treated in various ways than the corresponding Se-terminated surfaces. The results are related to solar-cell device performances, the primary application of these materials.

10:20am **TF+EM-MoM7 Preparation and Characterization of Transparent Conducting ZnTe:Cu Back Contact Interface Layer for CdS/CdTe Solar Cell***, U. Avachat, **N.G. Dhere**,* University of Central Florida

This paper presents preparation and characterization of transparent conducting ZnTe:Cu back contact interface layer for CdS/CdTe thin film solar cells for multijunction thin film PV applications. Polycrystalline ZnTe:Cu thin films were grown by Hot Wall Vacuum Evaporation technique. Hot wall set up was developed to obtain highly stoichiometric films with better material yield and thickness uniformity. 500 nm ZnTe:Cu films were prepared on glass and characterized for stoichiometry, structural properties and optical transparency by electron probe microanalysis, optical transmission spectroscopy and X-ray diffraction technique respectively. Highly stoichiometric ZnTe:Cu films were obtained on glass with optical transparency in the range of 70-80 % in near IR region. X-ray diffraction patterns revealed face-centered cubic phase of ZnTe with preferred {111} orientation. CdS/CdTe solar cells were completed with configuration, CdS/CdTe/ZnTe:Cu/ZnO:Al/Ni-Al and CdS/CdTe/ZnTe:Cu/ITO/Ni-Al. ZnO:Al and ITO thin film layers were deposited by RF magnetron sputtering and Ni-Al contact fingers were deposited by e-beam vacuum evaporation through metallic mask. Completed CdS/CdTe solar cells were characterized for their I-V characteristics using current voltage measurements.

10:40am **TF+EM-MoM8 CuPc:C60 Blend Film: A Photoemission Investigation***, **L. Lozzi**,* University of L'Aquila and INFM-CNR, Italy*; V. Granato,* University of L'Aquila, Italy*; S. La Rosa,* Sincrotrone Trieste Scpa, Italy*; S. Santucci,* University of L'Aquila and INFM-CNR, Italy

Recently a strong research effort has been devoted to study the application of organic-inorganic multiplayer films for the preparation of photovoltaic devices. Generally these devices are composed by a multilayer of an organic film which is the active layer, a charge acceptor (to reduce the electron-hole recombination probability) and the two metallic contacts to collect the charges (as ITO, Au and Al). The most used compounds are Copper Phthalocyanine (CuPc), as organic layer, and the C60, as electron acceptor. An improved system, showing an higher efficiency, can be prepared depositing, between the metallic contacts, a blend of active layer and charge acceptor. With this design one of the most important parameter, the exciton diffusion length (which is quite small in the organic systems), becomes less important because it is obviously much higher then the CuPc-C60 distance when these molecules are bonded. The realization of these blend films determines the strong reduction of the luminescence of the CuPc film, but it is not clear if in this blend film there is the formation of bonds between CuPc and C60 molecules or if its electronic structure is simply the sum of the electronic states of the two single compounds. In this contribution we will show the results obtained using soft X-ray photoemission spectroscopy on CuPc:C60 blend films, with different concentrations. These films have been deposited in ultra high vacuum by thermal evaporation. We will show a variation of the HOMO states as a function of the concentration ratio. This HOMO level moves towards the Fermi level, influencing the interface properties with the metallic contacts. The intensity and position of this level is strongly influenced by the CuPc:C60 ratio. This result could be related to the variation of the optical properties of these films.

11:00am **TF+EM-MoM9 Silicon Thin Films from Trichlorosilane for Electron Beam Recrystallized Solar Cells***, **C. Groth**, K. Ong,* Hamburg University of Technology, Germany

The project's aim is to produce polycrystalline thin film solar cells on low cost substrates, especially on float glass. The chemical processing is entirely dry, which leads to high efficiency and throughput. There is no size limitation using this sequence of processing; even the in-line production of complete solar panels is feasible. An intermediate Tungsten (W) layer of approximately 1 µm is used to maintain mechanical stability at high temperatures. Furthermore, it is used as diffusion barrier during the recrystallisation process and serves as back surface reflector and electrical contact. Two deposition processes are currently under investigation: DC-magnetron sputtering and plasma enhanced chemical vapour deposition (PECVD) using tungstenhexafluoride (WF@sub 6@) as precursor. Both processes are using substrate temperatures of ~400 °C. Analysis using XRD (x-ray diffraction) shows formation of @alpha@-W for sputtered layers while PECVD layers consist of @alpha@- and @beta@-W, depending on the process parameters. The silicon (Si) basis with a thickness of 15 µm is deposited by PECVD directly from trichlorosilane (SiHCl@sub 3@) as precursor at high rates of ~200 nm/min. Substrate temperature during the process is ~550 °C. RF frequencies of 13.56 MHz are used in both PECVD processes. P-doping of the basis is done in-situ using borontrichloride (BCl@sub 3@). The nanocrystalline silicon film is recrystallised by a line-shaped electron beam at high velocities of about 60 mm/s. This leads to grain sizes of up to several 100 µm. A PECVD deposited amorphous silicon layer will be used as hetero emitter to complete the solar cell.

11:20am **TF+EM-MoM10 Plasma-Assisted Co-Evaporation of Thin Films for Photovoltaic Applications***, S. Kosaraju, J.A. Harvey, **C.A. Wolden**,* Colorado School of Mines

This presentation describes the development of plasma-assisted co-evaporation (PACE) and its application to the formation of @beta@-In@sub 2@S@sub 3@ and InN thin films. The former is an alternative window layer for copper indium diselenide based devices and the latter is a potential absorber. In PACE metals are supplied by conventional thermal evaporation, while the chalcogen or nitrogen gas precursors are activated by an inductively coupled plasma (ICP) source. The performance of the ICP source to activate both H@sub 2@S and N@sub 2@ was measured and optimized using a combination of optical emission spectroscopy and mass spectrometry. Transport modeling was used to quantify the flux distributions of both the co-evaporated metal and the reactive species from ICP source impinging upon the substrate. The source geometries were positioned asymmetrically so that the influence of composition and absolute rate could be ascertained from a single deposition experiment in a combinatorial approach. Model predictions were compared and validated using measurements of film thickness, composition, and quality. Through the deposition of @beta@-In@sub 2@S@sub 3@ and InN it was demonstrated that PACE provides substantial improvements in both materials utilization and substrate temperature reduction. For the case of @beta@-In@sub 2@S@sub 3@ it was observed that film quality was highly sensitive to the S/In ratio. The buffer layer was formed as low as 100 °C, and it was found that both the morphology and optical band gap were strong functions of temperature. In the case of InN the most important parameter was the excitation of nitrogen in the ICP source. It was shown that the introduction of argon was beneficial to nitrogen activation as evidenced by measurements of crystal quality and electronic properties.

11:40am **TF+EM-MoM11 Anomalously High Seebeck Coefficient Observed in V@sub 2@O@sub 5@ Thin Films***, **S. Iwanaga**, N.T. Nguyen, R.B. Darling, F.S. Ohuchi,* University of Washington

Vanadium oxides, especially vanadium pentoxide (V@sub 2@O@sub 5@), have gained recent attention for a wide range of applications such as ion storage layers in solid-state batteries, windows for photovoltaic cells, and electro- and photo-chromic devices. Various transport properties have been investigated in the past; however, its thermoelectric properties have not been well characterized. Recently, we observed an anomalously high Seebeck coefficient from sol-gel deposited V@sub 2@O@sub 5@ thin films. Seebeck coefficients of between - 500 to - 700 µV/K were measured, with corresponding electrical conductivities ranging from 0.005 to 0.1 @ohm@@super -1@ cm@super -1@. Unlike conventional materials, the Seebeck coefficients and electrical conductivity act in parallel, suggesting that the carrier concentration increases while maintaining a high Seebeck coefficient. This peculiar transport characteristic appears to be related to polaron hopping. The power generation of the film was further estimated by current-voltage (I-V) measurements to assess the thermoelectric performance of the films. The I-V measurements were performed while applying a temperature gradient to the film by applying a current source in such a way that the thermopower current was suppressed by applying the current in the opposite direction. The I-V characteristics at different applied @DELTA@T were thus obtained, from which the output power (load characteristic, P) was calculated from the I-V data.

Applied Surface Science
Room 206 - Session AS-MoA

Electron Spectroscopies

Moderator: R.L. Opila, University of Delaware

2:00pm **AS-MoA1 High Resolution XPS and EELS of Assembled Organic Monolayers***, **J.-J. Pireaux**,* University of Namur, Belgium **INVITED**

Everyday application of XPS allows to unravel with quite simple procedures the elemental and chemical composition of materials surface in a quantitative way. Core and valence band spectra analyses do contain structural information as well : to gather it, high resolution analysis and sometimes study of reference materials are necessary. This will be demonstrated with the determination of the good-or-bad assembling property of some silane molecules with different hydrocarbon chain length deposited from a solution onto TiO@sub 2@ single crystals ; a model of the -Si-O-Ti-O- interfacial layer will be presented. While XPS and UPS synchrotron photoemission valence band analysis remain still qualitative for the determination of structural order, we will show that high resolution electron energy loss spectroscopy[(HR)EELS] can been successufully used to evaluate the crystalline domain size of alkane thiols layers assembled on gold surfaces ; indeed, the measure of the angular distribution of the scattered electrons corresponds to a diffraction experiment. With contributions of R. Magnée, Ch. Grégoire and A.-S. Duwez

2:40pm **AS-MoA3 Evaluation of Electron Back-scattering in Auger Analysis using a Cross-sectioned GaAs/AlAs Superlattice***, **M. Suzuki**, N. Urushihara, S. Iida, N. Sanada,* ULVAC-PHI, Inc., Japan*; D.F. Paul, J.S. Hammond,* Physical Electronics*; A. Yamamoto,* ULVAC-PHI, Inc., Japan

It is generally well known that when using electron excitation analysis techniques such as Auger electron spectroscopy, the analyzed volume is expanded due to the scattering effects in a solid surface region. We will present experimental results to evaluate generation of Auger electrons by inelastic scattered electrons. A cleaved cross-section of a GaAs/AlAs superlattice, consisting of three different thicknesses of repeating layers of GaAs/AlAs (50 nm/50 nm, 20 nm/20 nm, and 10 nm/10 nm) was analyzed with a scanning Auger Nanoprobe. Along the analyzed line perpendicular to the 50 nm thick-layers, the kinetic energy of the Al KLL Auger electrons varied by 5 eV to 6 eV, with a spatial distribution corresponding with the GaAs/AlAs superlattice structure. The amplitude of the Auger peak energy shift with beam position was smaller for the 20 nm-thick layers and almost negligible for the 10 nm-thick layers. The highest and lowest Auger energy positions correspond to the AlAs and GaAs layers, respectively. The analyzed surface was covered with a naturally oxidized layer, as the cleavage was carried out in air. The lower Al kinetic energy signal was detected when the electron beam hit the AlAs region, due to the reduction of aluminum oxide caused by electron beam.@footnote1@ The higher Al kinetic energy signal associated with aluminum oxide was generated by inelastically scattered electrons when the beam was at the GaAs region. These results will be discussed based on a model of electron scattering. @FootnoteText@ @footnote1@ M. Arai et al., O-32, The third international symposium on practical surface analysis (PSA-03), Korea, October 2003.

3:00pm **AS-MoA4 Angle Resolved XPS for Characterization and Metrology of Ultra-Thin Silicon Oxynitride Films***, **C.R. Brundle**,* C. R. Brundle & Associates*; G. Conti, Y. Uritsky,* Applied Materials, Inc.*; P. Mack,* Thermo Electron Inc., UK

The analytical tool set used in the wafer processing industry for metrology of thin films is changing because the films are becoming so thin and more complex. One of the new contenders for both characterization (the kind of detailed information needed in development, trouble shooting, and failure analysis) and metrology (rapid measurements of specific parameters on large numbers of samples) is XPS. Whereas many of the techniques used in the past become less effective as films become ultra-thin (0 to 50A range), XPS becomes most effective in this range. For the high k dielectric material, SiON, as used in the current generation of gate oxide production (10 to 30A), Angle Resolved XPS can provide very precise film thickness and at the same time, in principle, provide a depth distribution of the nitrogen dose using a constrained model to fit the data. Since the model fit to the data can never be unique the approach works best for two extremes: 1) when there are really gross differences in distributions between films and it is this qualitative difference one is looking for and 2) when there are multiple measurements available for films made under a given processing condition that give the same profile fit, and then multiple measurements under a different processing condition which give a consistently different fit (even if small), signifying that a change in profile has occurred. We present examples of both situations from current industry samples. The former is more of a film/process development issue and the latter is more of a metrology issue. It does seem possible to tell that small changes in distribution have occurred, even if one cannot fully quantify those changes. An interesting point is that in none of the many (hundreds)of samples studied, is a spike in the N concentration observed at the surface (first 2A) by ARXPS, unlike in some reports using TOFSIMS on similar samples.

3:20pm **AS-MoA5 Multi-Technique Characterization of Iron Nanoparticles***, **D.R. Baer**, M.H. Engelhard, C.M. Wang, K.H. Pecher,* Pacific Northwest National Laboratory*; R.L. Penn,* University of Minnesota*; P.G. Tratnyek,* Oregon Health and Sciences University*; Y. Qiang,* University of Idaho*; D.E. McCready, J.C. Linehan, J.E. Amonette,* Pacific Northwest National Laboratory*; J. Antony,* University of Idaho

Understanding the chemical properties of iron nanoparticles requires detailed information about the size, physical and chemical structure and the presence of surface coatings. Because of the reactive nature of iron, these particles are usually covered by some type of incidental or deliberately added protective layer. In spite of any protection, the properties of the particles change with time and are altered by the environments they have been exposed to and in some cases by the manner the samples have been handled prior to analysis. For some of our reaction studies, we expect the particles to react and change with time and it is important to understand this particle evolution. This presentation will describe aspects of nanoparticle synthesis and processing, the methods we are using to handle the samples, the priority and order of the analysis, and the information we expect from each method. Methods routinely used include: x-ray photoelectron spectroscopy; transmission electron spectroscopy; x-ray diffraction; surface area analysis; x-ray adsorption spectroscopy. These are correlated with measurements of electrochemical properties and chemical properties. The issues and challenges of forming a consistent picture of the particles as a function of time will be discussed.

3:40pm **AS-MoA6 Workfunction Differences between Cu Grains: Laterally Resolved UPS with the NanoESCA***, **J. Westermann**, D. Funnemann, B. Kroemker,* Omicron NanoTechnology GmbH, Germany

Recently, we have developed an Imaging XPS spectrometer with lateral resolution in the range of 200nm and below.@footnote 1,2@ This instrument has recently been used for the study of work function differences on a variety of samples. Main focus of this application was the work function variation between different copper grains. As copper is currently of great interest as a material for interconnects in semiconductor devices, the understanding of grain properties is a key for the improvement of the interconnect properties. Samples were provided by the Laboratoire d'Electronique de Technologie de l'Information (LETI, Grenoble). Using the NanoESCA, we can show for the first time the relation between secondary electron intensity and work function with a high spatial resolution. Surprisingly, this does not follow the Fowler plot as was expected previously.@footnote 3@ In addition, we show measurements on a heterogenous material combination with microstructured Gold patterns on a Silicon Oxide sample. These data demonstrate the powerful combination of imaging with spectroscopy: We identify regions of band-bending, charging and different work-functions. @FootnoteText@ @footnote 1@ Escher et al., J.Phys.:Condens. Matt 17 (2005) 1329-1338@footnote 2@ Escher et al., J. Electron Spectrosc. Relat. Phenom., 144-147 (2005) 1179-1182@footnote 3@ Przychowski et al., Surf. Sci. 549 (2004) 37-51.

4:00pm **AS-MoA7 In-Situ and Ex-Situ Characterization of the Electrochemically-Accelerated Corrosion of Ni-Cr-Mo-Gd Alloy Surfaces in Aqueous Media***, P.J. Pinhero, T.E. Lister, R.E. Mizia, **T.L. Trowbridge**,* Idaho National Laboratory*; A.W. Glenn,* Idaho Completion Project

A new thermal-neutron-absorbing structural Ni-Cr-Mo-Gd alloy was developed at the Idaho National Laboratory (INL). The purpose of this alloy is to potentially absorb neutrons liberated from spent nuclear fuel (SNF) and mitigate any issues related to nuclear criticality. The microstructure of this alloy indicates a two-phase structure consisting of the primary Ni-Cr-Mo austenite matrix phase and secondary Ni@sub 5@Gd phase inclusions arising from the precipitation of the austenite-insoluble Gd. Presently, this alloy is under consideration for use within the U.S. Department of Energy (DOE) standardized SNF waste packages. To support the case for this alloy's acceptance and understand its more fundamental surface character, studies were undertaken to examine its structure and composition with respect to its bulk properties, the role of oxidation and resulting passivation on its susceptibility to corrode, and finally how these properties are influenced through boron-doping. This paper focuses on the susceptibility of the Ni-Cr-Mo-Gd surface to corrode. Scanning electrochemical microscopy (SECM) was used to examine localized corrosion of the surface in situ. It was observed that the corrosion initiates at the interfaces between the Ni@sub 5@Gd particles and the surrounding austenite matrix. Corrosion then propagates such that these particles completely dissolve, leaving an intact "passive" Ni-Cr-Mo surface. Current-sensing atomic force microscopy (CS-AFM) images help support the argument of electron transfer initiating at the interface formed between the included particles and the austenite matrix. Ex situ analysis using focused ion beam / scanning electron microscopy (FIB/SEM), scanning Auger microscopy (SAM), and x-ray photoelectron microscopy show how the structure and surface composition change as a function of the electrochemically driven corrosion process.

4:20pm **AS-MoA8 Throughput Advantages of PRBS Modulation in TOF Electron Spectroscopy and Mass Spectrometry***, **R.H. Jackson,*** Stillwater Scientific Instruments*; Z. Yang,* Univ. of Maine*; L.J. LeGore, B.G. Frederick, P.H. Kleban, C.B.H. Crothers, D.P. Martin,* Stillwater Scientific Instruments

Pseudo-random binary sequence (PRBS) modulation is a method of multiplexing in the time domain to increase the time domain efficiency of an analyzer. We have combined PRBS modulation in a time-of-flight velocity analyzer with maximum likelihood signal recovery methods in both high resolution electron energy loss spectroscopy (HREELS) and mass spectrometry (MS). In previous TOF-HREELS measurements, we have decreased data acquisition times from hours per spectrum to a few minutes, while maintaining resolution in the 2-4 meV range. Although time-of-flight instruments typically trade improvements in time domain throughput for decreases in the etendue, the use of a Bradbury-Nielsen gate chopper allows our optical design to maintain large acceptance angles from the source while achieving high throughput and resolution. We characterize the throughput advantages of a broadband input lens for use in the TOF-HREELS analyzer. Similar advantages are achieved in our GC/MS implementation of a TOF mass spectrometer, compared to the state-of-the-art orthogonal acceleration TOF-MS configuration. We also report order of magnitude improvements in the time resolution and throughput of the timing and control electronics and computational capabilities for implementation of the data recovery algorithms.

4:40pm **AS-MoA9 Novel Field Emission Source for Electron Microscopy***, J.W. Lewellen, **J.R. Noonan,*** Argonne National Laboratory

A novel field emission electron source that combines desirable features of thermionic cathode and photocathode has been designed. Simulations indicate that the electron beam has very small emittance, ~ 2 nm-radian, and high average current. The emittance can be reduced to less than 0.01 nm-radian by taking beam slices, which also reduces the beam current. The source uses high gradient radio frequency (RF) fields to extract electrons off of a field emitter tip and accelerate these electrons to ~1.5 MeV energy. The resulting gun design show promise in a number accelerator and non-accelerator applications, such as energy recovery LINACS, TeraHertz radiation sources, high voltage electron microscopy, electron beam welding, and thin film deposition. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under contract No. W-31-109-ENG-38.

5:00pm **AS-MoA10 Differential Charging of Nanoparticles on Oxide Surfaces as Determined by XPS with External Stimuli***, U.K. Demirok, I. Tunc, **S. Suzer,*** Bilkent University, Turkey

By recording the XPS spectra while applying external d.c. and/or pulsed voltage stimuli, it is possible to control the differential charging, and extract information related with dielectric properties of various surface structures. We have carried out a number of experiments to determine the charging/discharging behavior of various surface structures consisting of Au, Ag, and Pt (metallic), Titania (semiconductor), and Silica (dielectric) both as they are and also as Core-Shell type Nanoparticles using XPS with external voltage stimuli. Differences and similarities of these structures with respect to their chemical compositions, and also with respect to the form (d.c., pulsed, etc.) of the voltage stimuli applied, will be presented and discussed in detail.

Biomaterial Interfaces
Room 313 - Session BI-MoA

Biomaterials and Neutrons (BioMaN) II

Moderator: M. Grunze, Universität Heidelberg, Germany

2:00pm **BI-MoA1 Effective Protein-Protein Interaction and Clustering Phenomenon in Solution Studied by Small-Angle Neutron Scattering***, **S.-H. Chen,*** Massachusetts Institute of Technology **INVITED**

The bottleneck of protein crystallography is the lack of systematic methods to obtain protein crystals, which is partly due to imprecise understanding of the physical chemistry conditions that control the growth of protein crystals. A general knowledge and comprehension of the effective protein-protein interaction potential in solution and the resulting phase behavior thus becomes essential. It has been shown that the crystallization curves of some globular proteins appear to coincide with the phase diagrams of a hard sphere system interacting with a short range attraction.@footnote 1,2,3@ Moreover, the study of the intensity distribution, I(Q), of some proteins measured with small angle neutron and X-ray scattering also suggests presence of a short-range attractive interaction between protein molecules besides the electrostatic repulsion induced by the residual charges in protein molecules.@footnote 4,5,6@ The so-called DLVO potential, which has been successfully applied in many colloidal systems, meets some successes when applied to protein solutions,@footnote 3,4,13@ but is still not enough to explain all the phenomena.@footnote 4,7,8,9@ Due to the complexity (anisotropic property, irregular shape, distributed charge patches, etc.), the full understanding of the properties of the effective interaction between protein molecules in solutions remains a challenge.@footnote 8@ Recent measurements of small angle neutron scattering (SANS) intensity distribution, in protein solutions by my group at MIT and others show some interesting results.@footnote 6,10,14@ First, besides the first diffraction peak, arising from the nearest neighbor inter-particle correlation in the liquid, there is an extra peak appearing at a much smaller scattering wave vector Q, due to the formation of well-ordered clusters inside the solutions. The appearance of this cluster peak is explained as due to the competition between the short-range attraction and the intermediate-range electrostatic repulsion in the effective protein-protein interaction potential in solution.@footnote 5,11,12@ Secondly, a rising intensity as Q approaching zero is observed in both liquid-like and solid-like samples, which can be shown to be due to the presence of another weak, very long-range attractive interaction term, in addition to the already proven short-range attraction and intermediate-range electrostatic HYPERLINK "mailto:repulsion.@footnote"repulsion.@footnote 12,14@ In this lecture, I shall show the results of a systematic SANS investigation of the clustering phenomenon and the newly found increasing low-Q intensity and its relation to the long-range interaction term. @FootnoteText@ @footnote 1@ D. Rosenbaum et al., Phys. Rev. Lett. 76, 150 (1996). @footnote 2@ M. H. J. Hagen et al., J. Chem. Phys. 101, 4093 (1994). @footnote 3@ G. Pellicane et al., J. Phys.: Condens. Matter 16, S4923 (2004). @footnote 4@ A. Tardieu et al., J. Cryst. Growth 196, 193 (1999). @footnote 5@ A. Stradner, et al., Nature 432, 492 (2004). @footnote 6@ B. Lonetti, E. Fratini and P. Baglioni., Phys. Chem. Chem. Phys. 6, 1388 (2004). @footnote 7@ M. L. Broide et al., Phys. Rev. E 53, 6325 (1996). @footnote 8@ R. Piazza, Curr. Opin. Colloidal Interface Sci. 8, 515 (2004). @footnote 9@ A. Striolo et al., J. Chem. Phys. 116, 7733 (2002). @footnote 10@ P. Baglioni, E. Fratini, B. Lonetti and S.H. Chen., J. Phys.: Condens. Matter 16, S5003 (2004). @footnote 11@ F. Sciortino et al., Phys. Rev. Lett. 93, 055701 (2004). @footnote 12@ Y. Liu, W.R. Chen and S.H. Chen., J. Chem. Phys. 122, 044507 (2005). @footnote 13@ C. F. Wu and S.H. Chen., J. Chem. Phys. 87, 6199, (1987). @footnote 14@ Y. Liu, E. Fratini, P. Baglioni, W.R. Chen and S.H. Chen (submitted to Phys. Rev. Lett.).

2:40pm **BI-MoA3 Small-Angle Neutron Scattering: A High Resolution, Non-Destructive Probe Of Biomacromolecular Structure***, **O. Byron,*** University of Glasgow, UK **INVITED**

Neutrons are of particular utility in the characterisation of biomaterials because of the large difference in their interaction with the @super 1@H nucleus compared with the @super 2@H nucleus. This allows contrast variation experiments to be performed in which certain components of complex biomaterials are made to be “invisible”. In addition, neutrons do not damage biomaterials in the same way as their x-ray counterparts may do. Small-angle neutron scattering has been used to successfully reveal the molecular architecture of a range of biomaterials. I will describe its use in several systems and will include the following areas: Diblock copolypeptides constructed via designed molecular self-assembly;

Nanomolecular architecture of biodegradable biopolymer inclusion bodies; Temperature response of dental-ceramics; Characterisation of medical biosurfaces resistant to biofouling

3:20pm **BI-MoA5 Determining the Structures of Peptides in Membranes Using Diffraction and MD Simulations*, S.H. White,*** University of California at Irvine **INVITED**

Quantitative structural images of peptides in oriented arrays of fluid lipid bilayers are necessary for interpreting thermodynamic measurements of peptide-bilayer energetics in molecular terms. Lamellar x-ray and neutron diffraction provide a starting point for obtaining structural images. But the high thermal motion of fluid bilayers limits "structures" to so-called bilayer profiles, representing a time-averaged projection of the unit-cell contents onto an axis normal to the bilayer plane. Specific deuteration of lipid structural groups combined with neutron diffraction difference methods allow these profiles to be decomposed into a collection of groups (phosphates, carbonyls, etc.) representing transbilayer probability distribution functions. The power of this method has been extended through the inclusion of x-ray data and a joint-refinement protocol. We have developed an x-ray method, referred to as absolute-scale refinement, that permits the determination of the disposition of peptides in fluid bilayers. These various approaches can used in concert as a powerful tool for gaining structural information. But that information is still only one-dimensional. We are now developing methods for obtaining experimentally validated three-dimensional structures by combining the diffraction methods with molecular dynamics simulations. In essence, our goal is to convert 1-D experimental data into 3-D images. Importantly, these images will be dynamic, which will permit the ensembles of peptide-lipid structures to be explored in detail. An essential issue, however, is the validation of MD simulations using diffraction data. A method of accomplishing this objective will be described. Research supported in part by grants from the National Institute of General Medical Sciences (GM46283 and GM68002) and the National Center for Research Resources (RR14812).

4:00pm **BI-MoA7 Exploring the Collective Dynamics of Lipid Membranes with Inelastic Neutron Scattering*, M.C. Rheinstädter,*** Institut Laue-Langevin, Grenoble, France **INVITED**

While most spectroscopic techniques, as e.g. nuclear magnetic resonance or dielectric spectroscopy, probe macroscopic responses, neutron and within some restrictions also x-ray scattering experiments give the unique access to microscopic dynamics at length scales of intermolecular or atomic distances. Only recently, it has become possible to study collective dynamics of planar lipid bilayers using neutron spectroscopy techniques.@footnote 1@ We determined the dispersion relation of the coherent fast picosecond density fluctuations on nearest neighbor distances of the phospholipid acyl chains in the gel and in the fluid phases of a DMPC bilayer. The experiments shed light on the evolution of structure and dynamics, and the relation between them, in the range of the gel-fluid main phase transition. The scattering volume restriction for inelastic neutron experiments was overcome by stacking several thousand highly aligned membrane bilayers. By combining different neutron scattering techniques, namely three-axis, backscattering and spin-echo spectroscopy, we present measurements of short and long wavelength collective fluctuations in biomimetic and biological membranes in a large range in momentum and energy transfer, covering time scales from about 0.1 ps to 150 ns and length scales from 3Å to about 1000 Å. A recent backscattering study gives information about slow molecular dynamics of lipid acyl chains and the 'membrane-water', i.e. the water molecules in between the stacked bilayers, in the nanosecond time range.@footnote 2@ The dispersion relations of the long wavelength undulation modes in lipid bilayers with nanosecond relaxation times can be determined by quasielastic reflectometry on spin-echo spectrometers and give direct access to the elasticity parameters of the membranes. @FootnoteText@ @footnote 1@ M.C. Rheinstädter, C. Ollinger, G. Fragneto, F. Demmel and T. Salditt, Phys. Rev. Lett. 93, 108107 (2004). @footnote 2@ Maikel C. Rheinstädter, Tilo Seydel, Franz Demmel and Tim Salditt, Phys. Rev. E, in print (2005), cond-mat/0501752.

4:40pm **BI-MoA9 Meeting the Challenges in Bio-Materials Research using Neutrons*, I. Anderson,*** Oak Ridge National Laboratory **INVITED**

When the Spallation Neutron Source, presently under construction in Oak Ridge, Tennessee, comes into operation in 2006 it will provide researchers across the world with unprecedented capabilities for the study of materials using neutron beams. A comprehensive suite of instrumentation is under construction to address new challenges in a wide range of disciplines including physics, materials science, environment, nanotechnology, biology and medical sciences. An overview will be given of the range of applications and promising new areas of research relevant to Biomaterial Interfaces with emphasis on the new capabilities provided by SNS.

DNA Topical Conference
Room 311 - Session DN+BI-MoA
DNA Detection and Sensing

Moderator: R.M. Georgiadis, Boston University

2:00pm **DN+BI-MoA1 Diamond-based Electrical Biosensors for DNA Detection*, B. Sun,*** *W. Yang, H. Kim, K.-Y. Tse,* University of Wisconsin-Madison*; J.N. Russell, Jr., J.E. Butler,* Naval Research Laboratory*; R.J. Hamers,* University of Wisconsin-Madison

The high stability of diamond makes an attractive material to use for interfacing microelectronics to biological molecules such as DNA. We have investigated the fabrication of diamond-based field-effect transistors in which the surface of the diamond is functionalized with biomolecules of interest, and binding to target molecules in solution produces a change in electrical properties via a field effect. Because the sensitivity depends on the size of the FET, our efforts have been placed on developing small devices, a few microns in size. Measurements in a field-effect transistor geometry can be compared to those made via impedance spectroscopy, as both are sensitive to the impedance of the diamond space-charge region. This talk will discuss the factors controlling the sensitivity and electrical stability of diamond-based electrical biosensing devices, as applied to DNA and other biomolecules.

2:20pm **DN+BI-MoA2 Polymer Replicated Interdigitated Electrode Arrays and Their Application in Multiparameter Molecular Diagnostics*, W. Laureyn*,** *J. Suls, K. Bonroy,* IMEC, Belgium*; G. Van Reybroeck, P. Jacobs, R. Rossau,* Innogenetics NV, Belgium*; P. Detemple,* IMM GmbH, Germany*; C. Van Hoof,* IMEC, Belgium

The development of DNA-sensor devices attracts substantial research efforts directed to gene analysis, detection of genetic disorders, tissue matching, forensic applications, etc. The electronic transduction of the formation of nucleic acid/DNA complexes using electrodes or semiconductors could provide quantitative information on the DNA-analyte in the sample. InterDigitated Electrode (IDE) arrays show great promise for the label-free detection of nucleic acid hybridization. However, the search for a technology that allows the manufacturing of thin-film IDE arrays on polymers in an easy and affordable fashion, which is compatible with state-of-the-art microfluidics integration technology, has received little attention to date. This paper reports on an innovative method for the affordable manufacturing of polymer based arrays of IDEs with µm dimensions. The reported fabrication process is based on a single and directional metal deposition on an appropriate three-dimensional structure, which is realized in a polymer material using micro-injection molding. The molds are manufactured by electroplating as a reverse copy of a silicon master structure. Using a well-designed combination of so-called microchannels and bumps, a self-contained shadowing effect can be achieved resulting in separated IDE structures after directional metal deposition. In this paper, we report on the full experimental proof-of-principle of the production of such devices and on their further integration in a functional micro-fluidic device. As a demonstrator application, we are currently investigating the label-free detection of post-amplification nucleic acid targets. Using planar 1µm IDEs on silicon, fabricated using deep-UV lithography, we were able to discriminate the hybridization of a 1 nM, 261-nt-long PCR-sample (exon 2 of HLA-DQB) down to a single-base mismatch level. A proof-of-principle on DNA-detection with the molded polymer structures is expected mid 2005.

2:40pm **DN+BI-MoA3 Surface Enzyme Reactions for Enhancing SPR Imaging Measurements of DNA Microarrays*, R.M. Corn,*** University of California, Irvine **INVITED**

The identification and application of bioaffinity interactions in a large scale array format has become an indispensable tool for modern biological research. Bioaffinity interactions such as DNA-DNA and DNA-protein interactions are now employed in an array format to quickly ascertain the presence of a particular DNA or RNA sequence in a sample, to detect and identify microbial and viral species, and to verify efficacy and function in medical diagnostics. In addition to the detection of DNA, microarrays are can be for the identification of new DNA-protein bioaffinity interactions such as and protein-protein binding. The surface-sensitive optical technique of surface plasmon resonance (SPR) imaging is a powerful "label free" measurement that can be used in an array format for the detection of bioaffinity interactions. SPR imaging detects the presence of a biopolymer on a chemically modified gold surface by the change in the local index of refraction that occurs upon adsorption. This talk will highlight the use of surface DNA enzyme reactions in conjunction with SPR imaging measurements to either provide enhanced biochemical selectivity or to amplify the optical response of the bioaffinity adsorption events. For example, we have recently used the enzyme RNase H to detect DNA adsorption onto RNA microarrays from femtomolar solutions. Further experiments on the reaction of Exo III with double-stranded DNA arrays and the use of Exo I with single-stranded DNA arrays will be employed to detail the kinetics of the surface enzyme reactions, which can be described with a combination of Langmuir and Michaelis-Menten concepts.

3:20pm **DN+BI-MoA5 Electrically Switchable DNA Layers as a Novel Detection Scheme for Bio-Sensing***, **U. Rant**, K. Arinaga, E. Pringsheim, M. Grubb,* University of Technology Munich, Germany*; S. Fujita, N. Yokoyama,* Fujitsu Laboratories Ltd., Japan*; M. Tornow, G. Abstreiter,* University of Technology Munich, Germany

Recently, we reported on the electrical manipulation of oligonucleotide layers tethered to gold surfaces.@footnote 1@ By applying alternating AC potentials to the supporting substrate, the orientation of the DNA strands can be dynamically switched with frequencies ranging up to the kHz regime, while the layer conformation is probed in real-time by optical means. Here we present the underlying principles governing the switchability of DNA layers and, in particular, how this novel functionality can be employed for multi-purpose, label-free sensing applications. In principle, the method can be utilized to detect any kind of (bio-) molecules that, upon specifically binding to the grafted probe layer will alter its switching behavior. As a unique feature, the technique allows to monitor the molecular dynamics of the electrically switched layers, which provides novel means to identify and characterize target-probe complexes on surfaces. We demonstrate the versatility and high sensitivity of the technique by the recognition of specific DNA sequences as well as the detection of a model protein system. @FootnoteText@ @footnote 1@ U Rant, K Arinaga, S Fujita, N Yokoyama, G Abstreiter, M Tornow; Nano Letters 4 (2004), 2441-2445

3:40pm **DN+BI-MoA6 DNA Conductance Sensor Platforms Using Nano-scale Break Junctions***, **A.K. Mahapatro**, K.J. Jeong, S. Bhattacharya, G.U. Lee, D.B. Janes,* Purdue University

For DNA sensors, a direct electrical readout of DNA selective binding events would enable integration of sensor elements with readout circuits. A possible readout approach involves measurement of the electrical conductivity of DNA strands bridging two narrowly spaced metallic contacts. In this work we describe few-molecule conductance measurements with electromigration-induced break-junctions (EIBJ). The double-stranded(ds) DNA oligionucleotide sequences are GGCGCGCGGGCGGGC-(CH@sub2@)@sub3@-SH-3', GGCGCAAAAACGGGC-(CH@sub2@)@sub3@-SH-3', and HS-(CH@sub2@)@sub6@-CGGAGAGTTGAGCAT-3', and their complements. Lithographically defined Au wires are formed by e-beam evaporation over oxidized silicon substrates silanated with (3-Mercaptopropyl)trimethoxysilane (MPTMS), then subjected to electromigration at room temperature to create nano-gaps. Although the Au wires are initially 2µm wide, gaps with length ~1nm and width ~5nm are observed after breaking, as observed through a field effect scanning electron microscope. ds-DNA was immobilized on the electrodes by assembling the DNA double-strands in an aqueous solution, reacting these solutions with the electrodes in solution, locking the double-helix configuration with a polycation, thorough rinsing with ultrapure water to remove any residual salt, and drying before measurement. The GC-rich, 3' thiol labeled DNA showed approximately 1Gohm resistance, but little conductivity was measured in the AT-rich or 5'thiol labeled DNA. This is consistent with single molecule conduction measurements where enhanced conductivity has been observed in GC-rich DNA. For the GC-rich DNA, higher conductivity is observed for devices immobilized in a higher concentration of salt (NaCl) in the standard phosphate buffer solution, which is attributed to more DNA-molecules immobilized between the electrodes. This study demonstrates that the EIBJ technique can be used to understand the electrical properties in nanometer scale materials such as DNA.

4:00pm **DN+BI-MoA7 Detection of DNA Hybridization on Porous Silicon Surface by Infrared Microspectroscopy***, **R. Yamaguchi**, K. Ishibashi, K. Miyamoto, Y. Kimura, M. Niwano,* Tohoku University, Japan

We propose a label-free method of detecting DNA hybridization by using porous silicon (por-Si) in conjugation with infrared (IR) microspectroscopy. In our method, DNA hybridization is detected through an analysis of infrared spectral profiles, and therefore fluorescence tags are not necessary for the hybridization detection. By using a por-Si film as the chip substrate, we can immobilize a great number of DNA molecules in a small surface area on the chip surface, since por-Si has a quite large effective surface area as compared to a flat Si surface. This may facilitate a high-sensitive detection of DNA hybridization on a small spot. In this study, we have investigated the feasibility of our method by measuring infrared absorption spectra of DNA molecules on por-Si film surfaces. We prepared a por-Si film with straight pores by anodizing a heavy-doped n-type silicon (100) wafer in a mixture of dilute hydrofluoric acid and ethanol. The diameter of straight pores was approximately 25 nm. Single-stranded DNA (target DNA) with 20 bases was immobilized on the por-Si film surface, and then the film surface was exposed to two kinds of probe DNA; one is complementary to the target DNA, and the other is not complementary to the target DNA. We utilized an IR microspectrometer to measure IR absorption spectra of the film before and after exposure to probe DNAs. The working area of the microspectrometer was set at 50Ã-50 Âµm2. For complementary DNA, we observed absorption peaks due to the probe DNA even after the film surface was rinsed with sodium chloride solution. For non-complementary case, on the other hand, no spectral changes were observed. These observations imply that DNA hybridization can be detected using IR microspectroscopy in conjugation with a por-Si based chip.

4:20pm **DN+BI-MoA8 Probing DNA-DNA Interactions between Cytosine (dC) Homo-Oligonucleotides Immobilized on Gold***, **A.M. Opdahl**,* National Institute of Standards and Technology*; D.Y. Petrovykh,* University of Maryland and Naval Research Laboratory*; H. Kimura-Suda,* National Institute of Standards and Technology*; L.J. Whitman,* Naval Research Laboratory*; M.J. Tarlov,* National Institute of Standards and Technology

We present experimental evidence for strong interactions between cytosine (dC) homo-oligonucleotides immobilized on gold surfaces. It is known that in neutral and acidic pH solutions (dC)-rich oligos can form multistrand structures [e.g. parallel strand, i-motif] via hemiprotonated (C+)(C) base pairing. For surface-immobilized DNA, we find evidence for the existence of these structures by probing the susceptibility of oligo(dC) films to displacement by 1-mercapto-6-hexanol (MCH) as a function of the buffer solution pH and ion composition. The premise of the method is that MCH is less effective at displacing any individual oligos within a film when strong DNA-DNA interactions are present. The structures and coverages of alkanethiol modified (-SH) and unmodified oligo(dC) films were characterized by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). Specifically, we find that (dC)@sub 25@-SH films are not displaced by MCH in neutral and acidic pH conditions that favor base-base (C+)(C) interactions, but are readily removed by MCH in mildly basic conditions. Both thiol modified and unmodified (dC) films exhibit higher resistance to MCH displacement in the presence of divalent buffer cations. This additional stability is attributed in part to electrostatic crosslinking of the negatively charged phosphate backbones. These results will be discussed along with the possibility of using (C+)(C) base pairing for stabilizing thiol-tethered DNA strands on gold.

4:40pm **DN+BI-MoA9 Quantification of Immobilized and Hybridized Oligonucleotide Surface Density on Commercial Amine-Reactive Microarray Slides using Radiometric Assay, Fluorescence Imaging and X-Ray Photoelectron Spectroscopy***, **P. Gong**, G.M. Harbers, D.W. Grainger,* Colorado State University

In an effort to establish a quantitative understanding of the correlation between immobilized probe DNA density on microarray surfaces and target hybridization efficiency in biological samples, we have characterized amine-derivatized, single-stranded DNA probes attached to amine-reactive commercial microarray slides and its complementary DNA target hybridization using fluorescence imaging, X-ray photoelectron spectroscopy (XPS) and @super 32@P-radiometric assays. Importantly, we have reproduced immobilization efficiencies of DNA probes under microarray formats using high ionic strength and increased DNA concentrations in macroscopic spotted dimensions to permit XPS surface analysis with good reliability and reproducibility. Target hybridization efficiency with complementary DNA was studied on these capture surfaces and shown to exhibit an optimum at intermediate probe densities. The macroscopic model provides a new platform for study of DNA surface chemistry using highly sensitive, quantitative surface analytical techniques. (e.g., XPS, ToF-SIMS) Sensitive @super 32@P-DNA radiometric measurements are now calibrated with more routine XPS DNA signals, facilitating future routine DNA density determinations without the use of hazardous radioactive assay. The objective is to provide new insight into the surface chemistry influences on DNA probe environments that influences the efficiency of target capture form solution in order to improve microarray assay performance.

5:00pm **DN+BI-MoA10 Ion Current Detection of Mono-nucleotide Passing into a Nano-hole Fabricated on Si Wafer***, **A. Oki**, Y. Horiike,* National Institute for Materials Science, Japan

D. Branton et al. demonstrated the electrical sequencing based on measurement of currents generated by passage of single-strand DNA into a 2 nm hole drilled in a cell membrane. But about 5 nm thick membranes do not allow discriminating single molecule of DNA with stacking spacing of 0.34 nm. For the goal, we have studied detection of currents generated from one base flowing into the nano-hole after cutting DNA to each base using a reaction of @lambda@exonuclease. The nano-hole was fabricated as follows: First, the KOH etching fabricated an anisotropic feature on the backside of the wafer through a 44 µm square Si@sub 3@N@sub 4@ mask, thus self-stopping at 31 µm depth. Then, the KOH etching opened an anisotropic feature on the upper side masked by a 5 mm square window, thereby forming a 360 nm diameter hole on the bottom of the upper side. 50 nm thick SiO@sub 2@ film grown on Si and subsequent CVD of 150 nm thick Si@sub 3@N@sub 4@ film filled periphery of the hole. Finally, 4.5 KeV Ar@super +@ ion irradiation removed the Si@sub 3@N@sub 4@ film on the hole position, thus fabricating the nano-size hole by monitoring instant increase of the ion current using a micro-channel plate set under the wafer. The hole size was not observed by SEM. To measure ion currents generated by mono-nucleotide passing the nano-hole, each 500 µM natural mono-nucleotide of dGMP, dCMP, dAMP, TMP was solved in a TE buffer solution, where a pair of a KCl saturated calomel was used as electrodes. Each ion current increased with increasing voltage. At 1.5V, ion currents of dCMP, TMP, dGMP, and dAMP were 45.9, 21.5, 15.5 and 13.8 nA, respectively. If the ion current varied inversely with molecular weight of mono-nucleotide, increases in order of ion currents are understood for dCMP and TMP. However present experimental accuracy must be checked for inverse characteristic of dGMP for dAMP because of small difference between both ion currents.

Electronic Materials and Processing
Room 309 - Session EM-MoA

High-k Dielectric Growth and Processing

Moderator: S.A. Chambers, Pacific Northwest National Laboratory and Univ. of Washington

2:00pm **EM-MoA1 Peter Mark Award Lecture: Synthesis and Patterning of Multifunctional Oxides***, **J.P. Chang**[1],* University of California, Los Angeles **INVITED**

The continuous down-scaling of the microelectronic and optoelectronic integrated circuits dictates the development of atomic layer deposition and high fidelity pattern transfer processes to synthesize and integrate novel materials, such as multifunctional oxides, into nanometer scaled devices. In this talk, I will first discuss current research progress in atomic layer deposition for synthesizing transition metal oxides which can be used as a gate dielectric material on semiconductors in transistors, or as a waveguide core material for planar miniature optical amplifiers. The interfacial composition and dipole are found to control the band alignment at the dielectric/semiconductor heterojunctions, while the short range order as determined by extended x-ray absorption fine structure analysis governs the electronic and optoelectronic properties. To integrate these oxide materials into future generations of devices, a viable etching process is needed to its realization. I will address the design of plasma chemistries to selectively pattern these oxide materials, including the individual and synergistic effects of ions and radicals, and their impact on device integration.

2:40pm **EM-MoA3 DFT Investigation of the Initiation of HfO@sub2@ ALD on H-Si(100)-2x1 and Nitrided Si Surfaces***, **Y. Xu**, C.B. Musgrave,* Stanford University

Atomistic mechanisms for the initiation of atomic layer deposition (ALD) of hafnium oxide (HfO@sub2@) on hydrogen terminated and nitrided silicon surfaces were investigated using density functional theory (DFT). There are two possible pathways for the reaction of the precursor Hf[N(CH@sub3@)@sub2@]@sub4@ and Si-H surfaces. One is to form a Si-Hf bond through a ligand exchange mechanism. One H atom from the Si-H* surface site and one N(CH@sub3@)@sub2@ group of the precursor combine through a four-centered transition state to form NH(CH@sub3@)@sub2@, which subsequently desorbs. The second pathway is one H atom will be transferred from Si-H surfaces to one CH@sub3@ group from precursor to form Si-N-Hf bond. Alternatively, Hf[N(CH@sub3@)@sub2@]@sub4@ and residual water in the reactor can react to form Hf[N(CH@sub3@)]@subx@(OH)@suby@. Subsequently, Hf[N(CH@sub3@)]@subx@(OH)@suby@ can react with Si-H* to form Si-O-Hf structures of the reacted precursor. This reaction is more kinetically favorable than both of the reaction of Hf[N(CH@sub3@)@sub2@]@sub4@ with Si-H surfaces and it is important for understanding the interface structure between silicon surface and HfO@sub2@ films. We have also investigated the reactions of Hf precursors with the nitrided Si(100) surface and found that alkylamide precursors can react with SiNH* sites to initiate ALD whereas HfCl@sub4@ reactions with the nitrided surface are kinetically unfavorable.

3:00pm **EM-MoA4 Hafnium Based High K Dielectrics for Advanced ULSI Technology***, **S. Muthukrishnan**, S. Kher, P. Narwankar, R. Sharangapani, T. Goyani, Y. Ma, K. Ahmed, G. Conti,* Applied Materials Inc.

Hafnium based high k dielectric has emerged as a primary candidate for advanced ULSI technology due to its thermal stability property and leakage current reduction potential in comparison to other high k materials. We have successfully developed a hafnium based gate dielectrics, HfO2 and HfSiOx, using both ALD and MOCVD techniques. The materials are thermally stable up to source/drain activation temperature of 1050C and above when nitrogen is incorporated into the high k film. The nitrogen is incorporated into the high k film through plasma nitridation. We have been able to incorporate as high as 25% nitrogen in the high k film. The benefit of the plasma nitridation is in its capability of engineering the nitrogen profile in the gate stack. The nitrogen can be engineered to maintain the highest concentration in the bulk of the film and prevent nitrogen from going to the dielectric and channel interface. This profile provided the High K film with low leakage current. X-ray Photoelectron Spectral analysis showed that nitrogen is primarily bonded to the silicon. Besides high k deposition, process integration is critical not only for the gate dielectric performance but also for its scaling capability. By controlling the silicon surface coverage prior to high k deposition and surface adsorption from clean room environment, additional scaling can be achieved with processing steps in integrated clustered tools.

3:20pm **EM-MoA5 Plasma-enhanced ALD for CMOS Applications***, **G. Wilk**, S. Marcus, P. Raisanen,* ASM America*; Y.M. Yoo, D.Y. Kim,* ASM Genitech **INVITED**

Plasma-enhanced ALD (PEALD) is a novel deposition technique which allows low-temperatures and a wide selection of precursors. PEALD films result in substantial leakage current benefit compared to thermal ALD films for dielectrics, and result in low-resistivity metals compared to thermal ALD metals. This process also maintains the benefits of standard Atomic Layer Deposition, including outstanding thickness control and conformality. Several applications will be shown to have excellent capacitance, leakage and breakdown characteristics, including metal gates and MIM capacitors. A range of dielectrics and metals will be presented, including Al2O3, HfO2, Ta2O5 and TiN.

4:00pm **EM-MoA7 LPCVD of Thin TiO@sub 2@ Films using TDEAT as Ti Source Gas and NH@sub 3@ as a Catalyst***, **X. Song**, C.G. Takoudis,* University of Illinois at Chicago

Thin TiO@sub 2@ films were deposited using Tetrakis(diethylamino)titanium (TDEAT) and O@sub 2@ as source gases, and NH@sub 3@ as a catalyst. The deposition temperature was 100 - 250°C and the system pressure was on the order of 1 torr. Real-time reactor gas analysis was carried out with a Residual Gas Analyzer. The TiO@sub 2@ film thickness was probed using spectroellipsometry. Time of flight secondary ion mass spectroscopy (ToF-SIMS) was utilized to study the depth profile of oxygen and other elements in the deposited films. The bonding states and atomic compositions of the samples were analyzed with

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[1] **Peter Mark Memorial Award Winner**

x-ray photoelectron spectroscopy (XPS). It is found that when the TDEAT feed flow rate increases, the TiO@sub 2@ deposition rate increases. The growth rate of TiO@sub 2@ films deposited using NH3 is substantially higher than that of films deposited without NH@sub 3@; for example, at 200°C, the growth rate increases from 4.7 nm/min (without NH@sub 3@) to 38 nm/min (in the presence of NH@sub 3@). XPS data show that the as-deposited Titanium Oxide films are stoichiometric, even when NH@sub 3@ is used. ToF-SIMS depth profile analysis of as-deposited and annealed TiO@sub 2@ is done using Cesium primary ion beam sputtering. The annealing is performed in Oxygen, at 750°C for 10 min. The Oxygen distribution profiles along the depth of both as-deposited and annealed films are found to be uniform; this indicates that Oxygen is incorporated during deposition rather than diffusion during annealing. The impurity levels of C, H, and N are found to be lower in the annealed films than those in the as-deposited films. This study shows that TiO@sub 2@ can be deposited at low substrate temperature and high deposition rates with low impurity levels using TDEAT and O@sub 2@ as source gases and NH@sub 3@ as a catalyst. The impurities in the films can be further reduced with post annealing if desired.

4:20pm **EM-MoA8 MOCVD of ZrO@sub 2@ Thin Films Using the Novel Single Precursor Zirconium 3-methyl-3-pentoxide, Zr(mp)@sub 4@***, W. Cho, K.-S. An, Y.K. Lee, T.-M. Chung,* Korea Research Institute of Chemical Technology, South Korea*; D. Jung,* Sungkyunkwan University, South Korea*; **Y. Kim,*** Korea Research Institute of Chemical Technology, South Korea

Thin films of zirconium dioxide, ZrO@sub 2@, have been deposited on silicon substrates by metal organic chemical vapor deposition (MOCVD) using the novel single precursor, zirconium 3-methyl-3-pentoxide {Zr[OC(CH@sub 3@)(C@sub 2@H@sub 5@)@sub 2@]@sub 4@, Zr(mp)@sub 4@}, with no additional oxygen source, and the CVD reaction mechanism was also investigated. In its thermogravimetric analysis (TGA), Zr(mp)@sub 4@ showed an excellent one-step weight loss and a low residual weight (less than 2.5%). The deposition rate was found to be ~30 Å/min at the substrate temperature of 400 °C and the activation energy of deposition was 33.3 kJ/mol which is similar to that of zirconium tert-butoxide, Zr(O@super t@Bu)@sub 4@. By gas chromatography/mass spectroscopy (GC/MS) and nuclear magnetic resonance (NMR) analyses of the thermally decomposed vapor phase products collected during the deposition of ZrO@sub 2@ films, it was clearly found that the films were grown via @beta@-hydrogen elimination processes of the Zr(mp)@sub 4@ single precursor. Negligible carbon contamination of the ZrO@sub 2@ films, examined by x-ray photoelectron spectroscopy (XPS), indicates that, except for the @beta@-hydrogen elimination processes, no additional decomposition and/or recombination processes contributed to the ZrO@sub 2@ film growth. The morphology, crystallinity, and electrical properties of the ZrO@sub 2@ films were characterized by atomic force microscopy (AFM), x-ray diffraction (XRD), and capacitance-voltage (C-V) and current-voltage (I-V) measurements.

4:40pm **EM-MoA9 The Effect of Nitrogen Incorporation on the Thermal Stability of La, Hf-aluminate Gate Stacks on Silicon***, **P. Sivasubramani**, P. Zhao, F.S. Aguirre-Tostado, J. Kim, M.J. Kim, B.E. Gnade, R.M. Wallace,* University of Texas at Dallas

The International Technology Roadmap for Semiconductors (ITRS) 2003 predicts the need for the introduction of high dielectric constant (k) gate dielectrics by 2006 to meet continued scaling requirements in metal-oxide silicon field-effect transistor (MOSFET) digital logic technology. Hf, Zr, group III or rare earth oxides with N, Al and/or Si additions have been identified as possible high-k gate dielectric candidates for near term MOSFET scaling.@footnote 1@ The thermal stability of a high-k dielectric film in direct contact with the underlying Si substrate is essential because out-diffusion of metal impurity atoms into the channel region during processing can cause carrier mobility degradation and affect the electrical performance of integrated circuit. Evaluation of the thermal stability of molecular beam deposited LaAlO@sub 3@ thin films show crystallization and out-diffusion of La and Al into Si (100) substrate when subjected to rigorous rapid thermal anneals (RTA) at or above 950 °C, 20 sec. in N@sub 2@ ambient.@footnote 2@ In this study, the effect of nitrogen incorporated into the La- and Hf-aluminate thin films and at the Si (100) interface will be discussed. Films are fabricated using reactive sputter deposition in Ar + N@sub 2@ followed by subsequent UV-O@sub 3@ oxidation at room temperature. High resolution transmission electron microscopy, atomic force microscopy, x-ray photoelectron spectroscopy, x-ray reflectivity, x-ray diffraction, and secondary ion mass spectroscopy are utilized to characterize the gate stacks before and after RTA in the 850 to 1050 °C temperature range. This work is supported by the Semiconductor Research Corporation (SRC) FEP Transition Center. @FootnoteText@ @footnote 1@ITRS, Front End Processes, p. 33 [2003].@footnote 2@P. Sivasubramani, M. J. Kim, B. E. Gnade, R. M. Wallace, L. F. Edge, D. G. Schlom, H. S. Craft and J.-P. Maria, accepted for publication in Appl. Phys. Lett.

5:00pm **EM-MoA10 Atomic Layer Chemical Vapor Deposition and Characterization of Hf-silicate, Hf-silicate/Al2O3, and Hf-silicate/SiO2 Gate Dielectrics***, **J. Kim**, K. Yong,* POSTECH, Korea

Silicate or aluminate including hafnium components is considered to be the most promising alternative gate dielectrics, due to good thermal stability in direct contact with silicon. Hf-silicate (HfSi@sub x@O@sub y@) films were grown by ALCVD using the precursor combination of tetrakis-diethylamido-hafnium [Hf(NEt@sub 2@)@sub 4@] and tetra-n-buthyl orthosilicate [Si(O@super n@Bu)@sub 4@]. A highly conformal, uniform Hf-silicate films of a few nm was observed by high resolution-TEM. The Hf/(Hf+Si) was average 0.38 for the bulk film, indicating a Si-rich composition. However, the formation of Hf-silicide (Hf-Si@sub x@) at Hf-silicate/Si interfaces was induced by the reaction of metallic Hf atoms with Si substrate atoms. As a gate oxide becomes thinner, the interfaces have shown to play a key role in device performance. In order to improve the interface properties, the Al@sub 2@O@sub 3@ and chemical SiO@sub 2@ layers were introduced to fabricate the Hf-silicate/Al@sub 2@O@sub 3@ and Hf-silicate/SiO@sub 2@ stacks, respectively. Al@sub 2@O@sub 3@ films were deposited by ALCVD at 200 @super o@C using Al(CH@sub 3@)@sub 3@ and H@sub 2@O. The chemical SiO@sub 2@ of ~1.5 nm was formed by phirana (H@sub 2@SO@sub 4@/H@sub 2@O@sub 2@=4:1) cleaning process. The Hf-silicate/Al@sub 2@O@sub 3@ bilayer showed amorphous characteristics, while Hf-silicate films showed a micro-crystalline structure. The Hf-Six formation was significantly decreased in the case of Hf-silicate/Al@sub 2@O@sub 3@ and Hf-silicate/SiO@sub 2@ bilayer. Compared with Hf-silicate, Hf-silicate/Al@sub 2@O@sub 3@ exhibited a lower leakage current density of 8.9 x 10@super -8@ A/cm@super 2@ at a gate bias of -1 V for an equivalent oxide thickness of 5.2 nm. Hf-silicate/Si and stacked Hf-silicate/SiO@sub 2@/Si were furnace annealed at 650, 750, and 850 @super o@C in the N@sub 2@O/Ar and N@sub 2@O/O@sub 2@ atmosphere. The phase transition (crystallization) was confirmed by XRD, FT-IR and Raman-IR results.

MEMS and NEMS
Room 207 - Session MN-MoA

Materials and Processes for Bio-MEMS and Bio-NEMS

Moderator: C.A. Zorman, Case Western Reserve University

2:00pm **MN-MoA1 Detection of Specifically Bound Biological Mass with Resonant Nanobeams and Nanochannels***, **S.S. Verbridge**, J.M. Moran-Mirabal,* Cornell University*; D.M. Tanenbaum,* Pomona College*; H.G. Craighead,* Cornell University

Nonlithographic techniques have been used for the fabrication of two types of nanostructures, used for detection of biological molecules. Polymeric electrospun fibers with dimensions on the order of 100 nm have been used in combination with photolithography to define free standing beams and channels, made of silicon nitride and glass, respectively. Beams are made by using electrospun fibers as etch masks, and channels by using fibers as a sacrificial core. Critical dimensions of both types of structure are hence determined by polymer nanofiber sizes. Nitride beams with resonant frequencies above 10 MHz, and quality factors above 10,000 have been used as binding sites for biological molecules. Nonspecific binding of proteins such as streptavidin to entire beams, as well as targeted binding using specific thiol linkages on gold binding sites (also defined with photolithography), have both been explored. These free standing nanobeams have been operated in resonance for the detection of the bound biological mass. Suspended glass channels have been used to observe fluorescence from labeled cellulase enzymes, at the single molecule level. Directions for using suspended nanochannels to do mechanical mass detection are also being explored, to make this sort of resonant nanostructure based mass detection technique more compatible with natural fluid systems of biological interest.

2:20pm **MN-MoA2 Optically Driven Nanomechanical Resonant Structures for Detection of Single Molecules***, **B. Ilic**, Y. Yang, K. Aubin, R. Reichenbach, J. Huang,* Cornell University*; S. Krylov,* Tel Aviv University, Israel*; H.G. Craighead,* Cornell University

Resonant nanoelectromechanical systems (NEMS) are being actively investigated as sensitive mass detectors for applications such as chemical and biological sensing. NEMS devices, made by lithographic techniques, can be formed in highly uniform arrays in a form that can be readily integrated with motion transduction and microfluidic systems. The types of materials that can be structured in this way have low mechanical losses providing a high mechanical quality factor of the oscillators and therefore well defined resonant frequencies. The very specific resonant frequencies and small mass of the oscillator allows for detection of small amounts of additional bound mass. Experimental investigations illustrate that the ability to engineer nanoscale features on the surface of NEMS devices, combined with localized chemical functionalization, allows for specificity and calibration of these devices as detectors. In our work, we have detected the binding of functionalized 1578 base pair long double-stranded disulfide modified double stranded DNA molecules to nanomechanical oscillators by measuring the resonant frequency shift due the added mass of the bound molecules. The resonant frequency of individual oscillators in an array of resonator devices was measured by thermo-optically driving the individual devices and detecting their motion by optical interference. Localized binding sites created with gold nanodots create a calibrated response with sufficient sensitivity and accuracy to count small numbers of bound molecules. The number of bound molecules on each device was quantified as proportional to the measured frequency shift with a proportionality constant determined experimentally and verified by modeling of the mechanical response of the system. For the smallest and most sensitive cantilevers the mass sensitivity was 194Hz/attogram.

2:40pm **MN-MoA3 Biofabrication: Enlisting Biological Materials for Fabrication***, **G.F. Payne**, L.Q. Wu, H. Yi, W.E. Bentley, J.N. Culver,* University of Maryland Biotechnology Institute*; G.W. Rubloff, R. Ghodssi,* University of Maryland **INVITED**

Biological materials offer unique properties that facilitate fabrication. Well-known are the self-assembly properties of biological materials that enable the bottom-up self-fabrication of nano-scale structures (e.g. nanowires and nanotubes). Yet, biological materials offer additional properties. They can be acted upon by enzymes enabling highly selective biocatalysts to be enlisted for enzymatic-assembly. And, biological materials often possess stimuli-responsive properties that enable a range of external stimuli to be enlisted for directed-assembly. We are studying the stimuli-responsive amino-polysaccharide chitosan as a versatile interface material. Chitosan's pH-responsive electrostatic properties allow its directed assembly (i.e. electrodeposition) in response to localized electrical signals that can be imposed from electrodes. Chitosan's directed-assembly can be controlled by controlling deposition conditions, and high lateral resolutions have been observed when the electrical signals are imposed from micropatterned electrodes. Once neutralized, the chitosan deposit is stable (chitosan is insoluble under neutral and basic conditions) although it can be re-solubilized by washing with mild acid. In addition to its stimuli-responsive properties, chitosan also offers chemical properties that permit the facile conjugation of proteins and nucleic acids to previously-deposited chitosan. These chitosan-bound proteins and nucleic acids can confer important functional properties (e.g. recognition, catalysis and binding). We are particularly interested in using the hybridization capabilities of chitosan-bound nucleic acids to serve as "nucleation sites" for the self-assembly of higher-ordered structures. Together, the results demonstrate that chitosanâ?Ts unique properties enable the integration of biological materials for biofabrication at the micro- and nano-scale.

3:20pm **MN-MoA5 Toward a Chitosan-Based Micromechanical Biosensor***, **S.T. Koev**, M.A. Powers, H. Yi, R. Ghodssi,* University of Maryland, College Park

In this work, the electrically deposited polysaccharide chitosan is used to biofunctionalize a microcantilever biosensor which detects the presence of target molecules on the chitosan as a shift in the resonant frequency of the cantilever. We have previously demonstrated the use of chitosan for spatially selective assembly of various biomolecules and now extend its functionality to a micromechanical sensor. Chitosan offers significant advantages over other materials commonly used for immobilization of biomolecules. The electrodeposition of chitosan would allow facile patterning of different probe biomolecules in sensor arrays. Additionally, chitosan's surface roughness, which can be controlled by the deposition conditions, leads to a large effective surface area for target molecule coupling. The microcantilever consists of layers of chitosan (100 nm), Cr/Au (110 nm), and Si@sub3@N@sub4@ (500 nm) fabricated on a Si substrate. The Au layer is used both for chitosan deposition and electrostatic actuation. The cantilever's resonant frequency is measured by actuating it at different frequencies and recording the amplitude with an optical profilometer in dynamic mode. Amine terminated ssDNA probe molecules are coupled to the chitosan amine groups using glutaraldehyde as a crosslinker and are hybridized with their complements. Resonant frequency measurements are performed after each of the following steps: chitosan deposition, addition of probe DNA, and addition of complementary target DNA. The data are analyzed to extract the surface mass density of DNA immobilized on the chitosan. The detailed fabrication, characterization, and measurement results will be presented.

4:00pm **MN-MoA7 Polymeric Intermediate Layer Bonding in Micro/Nano Devices at Low Temperature for Bio-MEMS/NEMS Applications***, **M. Dhayal**,* Dongshin University, South Korea

In this study using low pressure plasma polymerized thin intermediate layer bonding process the silicon-to-silicon and glass-to-glass substrate bonding in micro/nano devices was successfully carried out. This process has advantage for bonding of glass and silicon types of substrate materials al low bonding temperature up to 130oC. The bond strength was more than 2 MPa for an about 100 nm intermediate plasma polymerised acrylic acid, p-xylenne, styrene, 1-vinyl-2-pyrrolininne and allylamine intermediate layers on glass and silicon substrates. The intermediate plasma polymerised thin layer bonding strange was also tested for continuously more than 24 hours with changing the room temperature from 25 to 35 oC and bonding does not shows any problem. This bonding process has advantage in the micro/nano devices applications in biology where the control of surface properties is required and also this process allows the device to be reusable. In this study the fabrication of bio-MEMS was carried out using plasma polymerisation process with optical lithography, wet and dry etching techniques on silicon/glass substrate. An asymmetric electrode array used for micro pump in micro fluidic device with small electrode (4 Âµm wide) separated from the large electrode (20 Âµm wide) by 20 Âµm and 6 Âµm gaps in both sides respectively.

Nanometer-Scale Science and Technology
Room 204 - Session NS1-MoA
Nanotribology

Moderator: H.J. Mamin, IBM Research Division

2:00pm **NS1-MoA1 Scaling Effects in Tribology: Micro- and Macroscale Studies of Diamond Like Carbon Nanocomposite Coatings***, R.R. Chromik,* North Carolina State University*; **K.J. Wahl,*** Naval Research Laboratory

The formation of a transfer film is a key part of how solid lubricant and protective coatings provide low friction and resist wear. These interfacial films, or "third bodies," are found to be chemically and mechanically different from the original mating surfaces, and the evolution of contact behavior is tied intimately with their dynamic nature.@footnote 1,2@ While the role of transfer films in macroscopic contacts has received considerable study, the effects of scaling on friction, transfer film formation and dynamics remains largely uninvestigated. To this end, we have studied the microtribology of DLC nanocomposite coatings using a commercially available nanoindentation system. Reciprocating sliding tests at speeds of 1-4 µm/s were conducted using diamond and sapphire counterfaces having radii of 10 and 150 µm, respectively. These geometries resulted in two regimes of contact stresses: 0.25 to 0.85 GPa for sapphire and 1.5 to 5.5 GPa for diamond. The friction behavior as a function of contact stress was explored in the elastic regime. Microcontact friction behavior fit a Hertzian contact model over a broad load range. Diamond vs. DLC gave shear stress similar to macroscopic values@footnote 1@, while sapphire vs. DLC showed lower interfacial shear strength but higher friction overall. Ex situ optical microscopy, atomic force microscopy and micro-Raman spectroscopy suggest that friction response is correlated with formation of transfer films on the counterface. @FootnoteText@ @footnote 1@ T.W. Scharf and I.L. Singer, Tribology Letters 14, 3 (2003).@footnote 2@ I.L. Singer, S.D. Dvorak, K.J. Wahl and T.W. Scharf, J. Vac. Sci. Technol. A21, S232 (2003).

2:20pm **NS1-MoA2 The Effect of Filling Carbon Nanotubes on Their Tribological Behavior***, **S.-J. Heo**, S.B. Sinnott,* University of Florida

As microengineering technology continues to evolve, the design of MicroElectoMechanical System (MEMS) / NanoElectroMechanical System

(NEMS) devices is increasingly more complicated. At the same time, the need to consider the tribologicaly properties of the materials that are likely components in future MEMS/NEMS devices has increased. Carbon nanotubes are one of the candidate materials for use in NEMS due to their high stiffness in the direction of the nanotube axis, low Young's modulus perpendicular to the nanotube axis and relative ease with which they slide against one another in bundles as a result of their van der Waals interaction with each other. In addition, nanotubes can stand high compressive and tensile forces prior to failure due to their flexibility. Here we investigate the responses of a bundle of single-walled nanotubes (SWNTs) and filled SWNTs to compressive and shear forces between two hydrogen-terminated sliding diamond surfaces by using classical molecular dynamics simulations. After constructing the systems, they are allowed to equilibrate completely at the room temperature. Then, the topmost diamond substrate moves to compress the nanotubes and then slides relative to the lower diamond surface in order to shear the nanotube bundle. The forces on the atoms are calculated by using the reactive empirical bond-order (REBO) potential for hydrocarbons coupled to Lennard-Jones Potentials. The results elucidate the role of filling on the tribological responses of SWNT bundles. This work is supported by the NSF-funded Network for Computational Nanotechnology (grant no. EEC-02288390).

2:40pm **NS1-MoA3 Nanometer Scale Mechanical and Electronic Properties of Molecular Films*, M. Salmeron,*** Lawrence Berkeley National Laboratory **INVITED**

Molecular thin films are intensely studied in connection with applications in chemical recognition, molecular patterning and manipulation, molecular electronics and as tribological films to modify friction and adhesion in nano- and micro-scale devices. I will present studies aimed at understanding the relation between structure, mechanical stability and electronic properties of molecular films. Our studies reveal the strong interdependence between structure and properties and the role of externally applied pressure. Examples include Self-assembled and Langmuir-Blodgett films made of molecules with saturated alkane chains, aromatic and unsaturated bonds, oligothiophenes, etc.

3:20pm **NS1-MoA5 On the Influence of Structure on Friction: The Amorphous-Crystalline Transition in Antimony Nanoparticles*, C. Ritter,*** Humboldt University Berlin, Germany*; M. Heyde,* Fritz-Haber Institute of the Max-Planck Society, Germany*; K. Rademann,* Humboldt University Berlin, Germany*; U.D. Schwarz,* Yale University

This work addresses two of the crucial points in nanotribology, namely the dependence of friction on effective contact area and interface structure. As model system, antimony nanoparticles grown on graphite are used. Such particles can be easily prepared with different sizes, and the effective particle/substrate contact area can be deduced from scanning force microscopy images. Moreover, the particles are undergoing a structural transition from amorphous to polycrystalline during the growth process at about 10000-15000 nm@super 2@ in size. This feature can be used to establish a correlation between structure and friction. Antimony islands have been pushed over atomically flat substrate areas using the tip of a dynamic force microscope while the power dissipation necessary to move the islands was measured. To fully cover the amorphous-crystalline transition, to check on reproducibility, and to obtain sufficient statistics, 95 measurements including 57 islands (areas between 1370 nm@super 2@ and 112000 nm@super 2@) and four different cantilevers were performed. The threshold value of the power dissipation needed for translation of the crystalline islands depends linearly on the contact area between the islands and the substrate. With the assumption of a linear relationship between dissipated power and frictional forces, this implies a direct proportionality between friction and contact area. The amorphous islands, however, also fit with a linear law, but the slope is a factor of three lower than the one found for the larger particles, leading to significantly lower energy dissipation. This change and their tentative relation to the structural transition within the particles will be discussed.

3:40pm **NS1-MoA6 Combined Nanoindenter and Quartz Microbalance Studies of Realistic Tribological Contacts and Ultrathin Lubricant Films*, B. Borovsky*,** *A. Booth,* Grinnell College

For emerging technologies such as micromachined devices, it is increasingly important to understand high-speed, multi-asperity, microscale contacts lubricated with films as thin as a single molecule, and to control the effects of humidity. Most theoretical and experimental studies of small contacts do not directly access this physical regime. We have therefore used a combined nanoindenter and quartz crystal microbalance (QCM) to study the contact between a sapphire sphere and a polycrystalline gold electrode undergoing transverse shear at speeds on the order of 1 m/s. For the first time, we have used this combined system to study both dry and lubricated contacts, by applying monolayer octadecanethiol films. We have extended previous work@footnote 1@ by adding continuous monitoring of the QCM resonance bandwidth during indentations. We find that both the frequency and bandwidth of the QCM track changes in the contact area, as derived from the contact stiffness. Depending on the roughness of the gold electrode, variations in the frequency with contact area follow either the single-asperity or multi-asperity limits of the elastic no-slip model of the interface. However, this model fails to account for the large levels of dissipation observed during indentations and the dependence of the bandwidth on contact area. We attribute this to dissipation in outer portions of the contact subject to interfacial slip. We also report a reversible humidity effect whereby the levels of dissipation in lubricated contacts increase and decrease reproducibly with the amount of water incorporated into the octadecanethiol film. We will discuss refinements of the interaction model to account for frictional processes and the response of the polymer film to humidity, confinement, and high-frequency shear. Research supported by NSF, Research Corporation, and Hysitron, Inc. @FootnoteText@ @footnote 1@B. Borovsky, J. Krim, S.A. Syed Asif, and K. J. Wahl, J. Appl. Phys. 90, 6391 (2001).

4:00pm **NS1-MoA7 Effect of Temperature on the Nanomechanics of Lipid Bilayers Studied by Force Spectroscopy***, S. Garcia-Manyes,* ***G. Oncins****, F. Sanz,* University of Barcelona, Spain

The effect of temperature on the nanomechanical response of supported lipid bilayers has been studied topographically and by Force Spectroscopy with Atomic Force Microscopy. An AFM equiped with a high temperature stage heater has been used. It has been experimentally proved that the force needed to puncture a phosphatidylcholine lipid bilayer (yield threshold force, Fy)deposited on mica and tested in liquid environment is extremely temperature-dependent. The quantitative measurement of the evolution of Fy with temperature has been related to the structural changes (phase transitions)that the bilayer undergoes as observed through AFM images. These studies have been carried out with three different phosphatidylcholine bilayers that exhibit different main phase transition temperatures (TM), namely, 1,2-Dimyristoyl-sn-glycero-3-phosphocholine(DMPC), 1,2-Dipalmitoyl-sn-glycero-3-Phosphocholine (DPPC) and 2-Dilauroyl-sn-glycero-3-Phosphocholine (DLPC). The solid-like phase shows a much higher Fy than the liquid-like phase, which also has been proved to exhibit a jump (breakthrough) in the force-curve. Within the solid-like phase Fy decreases as temperature is increased, and suddenly drops as it approaches TM. Interestingly, a well in the Fy vs. temperature plot occurs around TM, thus proving an anomalous mechanical softening around TM. Such mechanical softening has been predicted by experimental techniques and also by MD simulations and interpreted in terms of water ordering around the phospholipid headgroups. A further temperature increase when the phospholipid bilayer is in the liquid phase does not change Fy significantly. Furthermore, ion-binding has been demonstrated to increase Fy@footnote 1@ and its influence on both solid and liquid phases has also been discussed. @FootnoteText@ @footnote 1@Garcia-Manyes,S.; Oncins,G.; Sanz,F.;(Submitted to Biophysical Journal).

4:20pm **NS1-MoA8 Understanding the Frictional Response of Organic Monolayer Coatings using Atomic Force Microscopy*, E.E. Flater,*** *R.W. Carpick,* University of Wisconsin-Madison

Motivated by the lack of fundamental understanding of friction, and that friction and wear are major limiting factors for surface micromachined devices, we use atomic force microscopy (AFM) to determine the nanoscale frictional properties of alkylsilane monolayers commonly used in these microscale devices to reduce adhesion and friction. Quantitative single asperity measurements of friction and contact stiffness are performed using SiO@sub 2@- and monolayer-terminated AFM tips on monolayer-terminated silicon. Using octadecyltrichrolosilane (OTS) and fluorinated monolayers (FOTAS), we observe that friction for these systems depends on the type of molecule and its packing properties. For the OTS monolayer there are two phases evident; the liquid condensed phase shows measurably lower friction at low loads than the liquid expanded phase, demonstrating that lower friction is associated with higher molecular packing density. However, the films exhibit the same frictional response at higher loads, indicating that compressed forms of both phases are tribologically equivalent. For FOTAS monolayer interfaces, fluorination increases friction at most loads, in agreement with measurements of micromachined interfaces. We find that frictional variation, as well as overall friction and adhesion for monolayer-coated tips are significantly reduced as compared with uncoated tips. Thus, the behavior of uncoated tips is highly dependent on the scanning history. This has wider importance for the acquisition of reproducible AFM nanotribology measurements in general, and strongly suggests that AFM researchers should strive to characterize and control the chemistry and structure of their tips to obtain meaningful measurements. We acknowledge Robert Ashurst for preparing the OTS samples, and Maarten de Boer and Alex Corwin for providing the FOTAS samples and microscale friction coefficients.

4:40pm **NS1-MoA9 The Observation of Nanoscale Melting at Sliding Interface***, **S.M. Lee**, J. Krim,* North Carolina State University

Tribological phenomena occurring at buried interfaces undergoing shear are extremely difficult to characterize experimentally, especially since the characterizations must ideally be performed at both atomic length and time scales. We report here one such investigation, involving a scanning probe tip sliding along the metal film electrode of a quartz crystal microbalance (QCM). The atomically sharp STM tip allows the generation of the nano-scale interface area while the sharp resonance of QCM allows measurement of the interaction forces applied to its surface. This in turn yields fundamental information on energy dissipation mechanisms associated with the sliding. For a W-tip sliding along a copper surface, we have observed nano-scale melting that is attributable to the rubbing action of the tip. As the rubbing velocity at the interface increases, the frequency shift converted from the positive to the negative when the interface area melts. Additionally, QCM amplitude shifts are enhanced by ~ 5 times upon melting of the interface. This observation implies that the nano-scale local temperature can be controlled by the rubbing velocity at the film-tip interface. And the temperature rise by rubbing can easily go over 1000°C, since the melting point of copper is 1084.62°C. The experimental results will be discussed with in the context of an extended Laschitsch and Johannsmann (LJ) model.@footnote 1@ @FootnoteText@ @footnote 1@ B. Borovsky, J. Krim, S. A. Syed Asif, and K. J. Wahl, J. Appl. Phys., 90, 6391 (2001)@footnote *@ This work has been supported by the DOE and the AFOSR Extreme Friction MURI program.

5:00pm **NS1-MoA10 Quantitative Elastic and Electromechanical Imaging: The Probe Dynamics of Vector Piezoresponse Force Microscopy***, **S. Jesse**, A.P. Baddorf, S.V. Kalinin,* Oak Ridge National Laboratory

Piezoresponse Force Microscopy (PFM) is a nanoscale probe of the local coupling of electronic and mechanical properties, including domain imaging, polarization switching, hysteresis measurement, and orientation imaging of ferroelectric and piezoelectric materials. The image formation mechanism in PFM is controlled by the voltage dependent mechanics of the tip surface junction and the dynamics of the cantilever. A detailed analysis of the nanoscale tip-surface junction electromechanics junction shows that, for a conductive tip, the PFM signal is independent of tip shape, as in case for Atomic Force Acoustic Microscopy (AFAM). We analyze the frequency and DC bias dependent dynamic response of vector PFM, in particular, the transmission of vertical, lateral, and longitudinal surface vibrations to the tip, using modeling and 2D frequency-bias spectroscopy. We demonstrate that for an electrical tip excitation, the contact resonances are determined solely by the elastic properties of the material. Therefore, the tracking of contact resonance frequency permits local mechanical characterization, absent the numerous stray resonances inherent to piezo-actuators used in AFAM. The frequency dispersion of the nulling bias, the DC bias at which the measured response to AC excitation is zero, yields a measurement of electrostatic vs. electromechanical contrast. The differences between transduction for vertical and in-plane response components are analyzed. It is shown that lateral PFM imaging is optimal at low frequencies, while vertical PFM is best at high frequencies where dynamic stiffening reduces the electrostatic and longitudinal contributions. Finally, we discuss the measurements of all three components of the electromechanical response vector using a single PFM scan. Implications for molecular orientation imaging are also discussed. Research was performed as a Eugene P. Wigner Fellow (SVK) at ORNL, managed by UT-Battelle, LLC under DOE contract DCE-AC05-00OR22725.

Nanometer-Scale Science and Technology
Room 210 - Session NS2-MoA

Nanometer Scale Assembly

Moderator: D.W. Carr, Sandia National Laboratories

2:00pm **NS2-MoA1 Seeing SAMs***, **R.G. Nuzzo**,* University of Illinois, Urbana-Champaign **INVITED**

We have begun a new program that exploits optics as a tool for exploring complex forms of surface chemistry. In this talk, I will describe the progress made in our recent work in this area, one that exploits the use of SAMs in several areas of technology. Of particular interest in this regard is the development of new SAM-based assembly systems-and chemistry for their modification-that allows their use as a platform for array-based proteomic assays. I will highlight in this presentation recent work that has led the development of new protocols-ones exploiting assembly, surface modification, soft lithography, and microscopy-that possess considerable potential for chemical sensing. The enabling of label free detection of protein binding events using non-spectroscopic methods of detection based on new imaging protocols will be discussed. The hope for SAMs, in this context then, is to demonstrate that seeing is believing.

2:40pm **NS2-MoA3 Directed Assembly and Separation of Self-Assembled Monolayers Via Electrochemical Processing***, **T.J. Mullen**, A.A. Dameron, J.R. Hampton, P.S. Weiss,* The Pennsylvania State University

We have directed separation in self-assembled monolayers (SAMs) on Au{111} using electrochemical desorption and characterized them with scanning tunneling microscopy (STM) and voltammetry. Separated domains of 1-dodecanthiolate were created by solution insertion into 1-adamantanethiolate SAMs. The adamantanethiolate domains were selectively desorbed by applying a reductive potential. Subsequently, the samples were immersed in 1-octanethiol solution, thereby producing SAMs with separated domains of dodecanthiolate and octanethiolate. We have investigated the molecular order of each lattice type with STM. The apparent height difference in the STM images and the two distinct cathodic peaks observed with voltammetry indicate distinct separated domains. The fractional coverages of each lattice before and after electrochemical desorption were calculated using both STM images and voltammograms. Using this electrochemical process, high-resolution chemically patterned surfaces with application in areas ranging from microelectronics to biocompatible systems have been assembled and characterized with molecular precision.

3:00pm **NS2-MoA4 AFM Investigation of the Growth of Self-Assembled MOSUD Layers***, **T.Y. Shih**, B.E. Koel, A.A.G. Requicha,* University of Southern California

Designed fabrication of structures on a nanometer scale often requires progress in the efficiency and control in deposition of self-assembled monolayers, especially in an approach that we have called layered nanofabrication (LNF). We report results demonstrating controlled growth of layers of (10-carbomethoxydecyldimethylchlorosilane) MOSUD that are used for embedding and planarizing patterns of Au nanoparticles. These studies of the growth of self-assembled monolayers of MOSUD extend previous investigations of modification of silicon surfaces by silane adsorption. In particular, we studied the influence of an anchor layer for stabilizing the Au nanoparticles. Atomic force microscopy (AFM) was used ex-situ to characterize the formation and quality of self-assembled mono and multilayers. In addition, ellipsometry was used to monitor the MOSUD film thickness and characterize the film growth mode. Growth of layers with a uniform packing and constant height could be obtained and the film thickness could be increased without covering the Au nanoparticles.

3:20pm **NS2-MoA5 Submicron Dispersions from Urea-Based Liquid Crystalline Phases***, **C. Fong**,* CSIRO Molecular Science, Australia*; J. Booth,* RMIT School of Applied Sciences, Australia*; C.J. Drummond, I. Krodkiewska, D. Wells, P.G. Hartley,* CSIRO Molecular Science, Australia

Surfactant self assembly phases such as micelles, vesicles / liposomes, and lyotropic mesophases are of technological importance as carriers for cosmetic formulations, as drug delivery systems, and as protein crystallisation media. Lyotropic mesophases offer particular advantages since under certain conditions they are robust to dilution, temperature and composition. The three dimensional structure also enhances solubilisation of hydrophilic and/or hydrophobic moieties when compared to their liposomal analogues. There are currently a limited number of materials which exhibit dilutable mesophase behaviour. Our aim was to design surfactants capable of self assembling into higher order surfactant liquid crystalline phases, which would be stable to dilution over a broad temperature range. In this study we have explored the urea based surfactants since the conventional wisdom suggested that this class of compounds was unable to form liquid crystalline phases. This work negates this long held view and demonstrates for the first time that surfactant mesophases with the urea head group are favoured by highly splayed hydrophobes with exaggerated cross sections. Hydrophobes such as hexahydrofarnesyl and phytanyl were successful in promoting room temperature inverse hexagonal phases which are stable against dilution and robust for a large temperature and composition regime. The current synthesis strategy has therefore more than doubled the previously known numbers of compounds with these properties. Colloidal dispersions of the bulk inverse hexagonal phase were prepared with average particle size < 300 nm. These nanoparticles have much reduced viscosities over the bulk phase with high surface area and the benefit that the bulk structure has been preserved. Significantly, they are of a suitable size range for applications such as intravenous drug delivery or bioremediation.

3:40pm **NS2-MoA6 Nanometer-scale Structures Created using Molecular Self-Assembly for Building Blocks and Components***, **M.E. Anderson**, C. Srinivasan, R. Jayaraman, E.M. Carter, M.W. Horn, P.S. Weiss,* The Pennsylvania State University

Molecular self-assembly plays an important role in the development of many nanolithographic techniques acting as building blocks and/or an active components for nanometer-scale devices. We have utilized self-assembled multilayers in conjunction with conventional lithography to create metal electrode structures with precise proximal placement in the 10-50 nm regime.@footnote 1-3@ By controlled placement and thickness of these multilayers (building blocks), the spacing between the electrodes can be fabricated with single nanometer resolution. Much effort has gone into developing the lithographic process steps to create precise nanometer-scale gaps reproducibly with electrical integrity.@footnote 4@ We will present methods relevant to the processing parameters and data regarding the electronic characterization of these nanogaps. The optimization of lithographic processes compatible with self-assembly has opened a novel avenue for directed chemical patterning of multi-component self-assembled films. The multilayers themselves are interesting complex nanometer-scale materials; studies are underway to understand and to manipulate their formation and electrical properties. We continue to push this technology toward architectures relevant for device fabrication; these techniques will be discussed. @FootnoteText@ @footnote 1@ A. Hatzor and P.S. Weiss, Science 291, 1019 (2001).@footnote 2@ M. E. Anderson et al., Journal of Vacuum Science and Technology B 20, 2739 (2002).@footnote 3@ M. E. Anderson et al., Journal of Vacuum Science and Technology B 21, 3116 (2003).@footnote 4@ M. E. Anderson et al., MicroElectronic Engineering, in press.

4:00pm **NS2-MoA7 Electric Nanocontact Lithography to the Directed Self-Assembly of Nanoparticle Based Devices***, C.R. Barry, A.M. Welle, U. Kortshagen, S. Campbell, **H.O. Jacobs**,* University of Minnesota **INVITED**

The first part of this talk will review recent results in the area of Electric Nanocontact Lithography while the second part will discuss the use of electrostatic forces to direct the assembly of nanomaterials. First we report on a programmable, reconfigurable, printing approach for parallel nanofabrication of three different types of structures: patterns of charge, oxide, and e-beam sensitive resist. Our approach that we refer to as Electric Nanocontact Lithography (ENL) is based on previous knowledge in the area of conducting scanning probe lithography which uses a conducting probe to electrically expose and modify a surface. ENL makes use of the same physical principles; however, instead of using a single electrical point contact, we use programmable electrical nanocontacts of different size and shape to expose a surface. In the second part we report on a novel directed self-assembly process to assemble nanoparticle based devices. Nanoparticles are considered potential building blocks for the fabrication of future devices. The use of nanoparticles and nanomaterials in general, however, requires novel assembly concepts. The concept that we present is based on electrostatic interactions. In particular we demonstrate directed self-assembly of nanoparticles onto charged surface areas (receptors) with 40 nm resolution. A liquid-phase assembly process where electrostatic forces compete with disordering forces due to ultrasonication has been developed to assemble nanoparticles onto charged based receptors in 10 seconds. A gas-phase assembly process has been developed that uses a transparent particle assembly module to direct and monitor the assembly of nanoparticles from the gas phase. A process is also being developed to enable the patterning of any organic and inorganic nanomaterials with sub 100 nm resolution. First patterns of bio-molecules will be presented. Currently, the electrostatically directed assembly of sub 10 nm sized proteins, 10 - 100 nm sized metal, 40 nm sized silicon nanocubes, and 30 nm - 3000 nm sized carbon nanoparticles has been accomplished. The application to nanoparticle devices will be discussed and first results on a nanoparticle transistor will be presented.

4:40pm **NS2-MoA9 Self-Assembly Activated by Molecular Motors***, **H. Hess**,* University of Florida*; J. Clemmens,* University of Washington*; C. Brunner,* ETH Zurich, Switzerland*; R. Doot,* University of Washington*; S. Luna,* ETH Zurich, Switzerland*; K.-H. Ernst,* EMPA Duebendorf, Switzerland*; V. Vogel,* ETH Zurich, Switzerland

In molecular self-assembly, the transport of the interacting parts is typically diffusive, and thermal forces prevent the mismatched assembly of non-complementary parts. This situation has serious disadvantages: Diffusive transport slows as building blocks become larger, thermal forces are distributed over a wide range which is difficult to adjust, and thermal forces strain even correctly assembled connections. Active transport on a molecular scale, for example powered by biomolecular motors, can overcome these disadvantages and provide strong, tunable, and directed forces which facilitate the ordered assembly of supramolecular structures. Furthermore, the assembled structures can be under internal strain and internally ordered without representing a minimum energy configuration. As a consequence of the transport properties of the system a high degree of long-range order can emerge. We experimentally demonstrated such a self-assembly system relying on active transport of functionalized microtubules by kinesin motor proteins.@footnote 1@ @FootnoteText@footnote 1@ Hess, H.; Clemmens, J.; Brunner, C.; Doot, R.; Luna, S.; Ernst, K.-H.; Vogel, V., Molecular self-assembly of "Nanowires" and "Nanospools" using active transport. Nano Letters 2005, 5, (4), 629-633.

5:00pm **NS2-MoA10 Directed Assembly and Real-Time Electrical Detection of Nanowire Bridges***, **L. Shang**, M. Marcus, J. Streifer, B. Li, R.J. Hamers,* University of Wisconsin-Madison

We have explored the use of dielectrophoretic manipulation combined with biomolecular recognition to control bridging of individual metallic and semiconducting nanowires across micron-sized electrical gaps. While dielectrophoretic manipulation is only temporary, more permanent assembly can be achieved using biomolecular recognition. For example, while biotin-modified nanowires interact only weakly with bare Au electrodes, they bind strongly to avidin-modified electrodes. The bridging of a nanowire across the gap can be detected electrically even though the nanowire is spaced away from the gold contact by the biomolecular contact. We have develop a novel method for achieving real-time monitoring of nanowire bridging events, using one AC electric field to manipulate the wires and a second field to measure the changes in electrical response induced by nanowire bridging. Because the change in electrical response is primarily capacitive, detection of bridging events is most sensitively achieved at higher frequencies, on the order of 1 kHz-100 kHz. At a fixed measurement frequency, we observe a step-like increase in current when a nanowire bridges the electrodes. Individual silicon and metal nanowires can be detected visually as well as electrically, allowing visual confirmation of the origin of the electrical response.

Plasma Science and Technology
Room 302 - Session PS1-MoA

Dielectric Etch I

Moderator: H. Maynard, IBM

2:00pm **PS1-MoA1 Reduction of Line Edge Roughness for 65nm Technology Node for Etched Contact Holes***, **B. Goodlin**, D. Farber, T. Lii, G. Shinn,* Texas Instruments Incorporated

For the 65nm technology node, reduction of contact hole line edge roughness is critical for reliable performance in densely packed memory cells. Origins of contact line edge roughness are attributable to three different mechanisms: 1) pattern transfer line edge roughness, resulting from propagation of striations from 193nm resist to the underlying substrate, 2) deposition-related line edge roughness, resulting from pattern transfer of non-uniform and irregular shaped deposition at the top of the hole to the bottom of the etched feature, and 3) pin-hole punch-through line edge roughness, where faceting or thinning of resist towards the end of etch processing results in shallow pin-holes that do not propagate down the entire length of the feature being etched. In order to fully appreciate these different types of line edge roughening for process optimization, a metrology technique was utilized that could characterize roughness at both the top and bottom of an etched feature. Using such metrology, an etch process has been optimized to minimize line edge roughness, while satisfying several other strict processing constraints.

2:20pm **PS1-MoA2 Difference in Etch Depth between Isolated and Dense Holes in Via-Etching of SiOC Film***, **Y. Momonoi**,* Hitachi, Ltd., Japan*; K. Yonekura,* Renesas Technology Corp.

Carbon doped silicon oxide (SiOC) has been widely used in integrated circuits (ICs) in order to reduce the total resistance capacitance (RC) delay in the interconnects. However, we found that there was a significant difference between the etch depths of isolated and dense SiOC via-holes. In addition, we found a mutually opposite dependence of etch depth on pattern density under different etching conditions. Equally, the etching properties, e.g., etch rate and depth of unexpected etch stop that are dependent on pattern density were different in different etching conditions. We expect that the difference in etch depth is a key issue in controlling critical dimensions, mask selectivity, and erosion of etch stop layers. In investigating the difference, it was clarified that the etch depth of isolated patterns was deeper than that of dense patterns when the etch depth was determined by an unexpected etch stop (narrow etch-stop-margin condition), and that the etch rate of isolated patterns was slower than that of dense patterns when the etch depth was based on etch rate (wide etch-stop-margin condition). We also found that the difference increased the longer the wafers were stored, which is in accordance with an increase of a gas degassed from SiOC in thermal desorption spectroscopy. We therefore investigated the influence of the gas on SiOC etching by adding it to plasma. Consequently, the added gas resulted in the same difference in etch depth as the difference that occurred between isolated holes and dense holes in both etch-stop-margin conditions. These results indicate that more of the gas degassed from isolated holes in SiOC determines the difference in etching depth.

2:40pm **PS1-MoA3 Etching Mechanisms of Low-k Material with the Solid First@superTM@ ILD Process in Fluorocarbon based Plasma***, **T. Chevolleau**, D. Eon, M. Darnon, L. Vallier, O. Joubert,* CNRS/LTM, France

In CMOS technology, most of the interlayer dielectric materials achieve low k value by introducing porosity in order to reduce the total resistance capacitance (RC) delay in the interconnect levels. However, porous materials as pSiOCH are very sensitive to ash and etch plasma exposure and one of the integration challenges is to reduce the impact of these plasma processes. To solve this issue, one of the emerging solutions is the Solid First@superTM@ ILD process. In this approach, the porosity in SiOCH is generated by releasing porogens (carbon based polymer) after patterning or copper filling. The SiOCH containing porogen materials are expected to behave like non-porous materials during the etching and ashing processes (as long as the porogens have not been released). This study concerns the etch mechanisms of a solid first SiOCH low-k (Zirkon V8@super+@ from Rohm and Haas) and selectivitiy to SiC and SiCN etch stop layer. The etching is performed on blanket wafers in an industrial MERIE reactor (Magnetically Enhanced Reactive Ion Etcher) using fluorocarbon based plasmas. Etch rates are measured by ellipsometry, chemical surface composition is analyzed by quasi in-situ XPS, and bulk modification by infrared spectroscopy. Etching is performed in fluorocarbon based plasmas (CF@sub4@) in mixture with Ar, CH@sub2@F@sub2@, or O@sub2@). Similarly to dense SiOCH materials, the etch rate decreases with either increasing Ar dilution or polymerizing gas addition. Nevertheless, XPS analyses reveal that the increased carbon content in the low-k material due to the presence of the porogen leads to the formation of a thick fluorocarbon overlayer during plasma exposure. Consequently, etch stop phenoma can occur even with low polymerizing fluorocarbon plasmas. On the other hand, FTIR analyses clearly show that the presence of porogens in the SiOCH matrix prevent bulk modification during a fluorocarbon plasma exposure.

3:00pm **PS1-MoA4 The Role of Inert Diluents in Low Pressure Electronegative Fluorinated Gas Discharges under Dual Frequency Excitation***, **M. Hussein**, M. Abdelrahman,* Intel Corporation

We investigated the role of argon (Ar) and helium (He) dilution on the discharge characteristics and etch rate performance of NF3 plasma under single and dual excitation frequency conditions. The discharge complex impedance was measured using an advanced, passive I-V probe installed between the match network and the bottom electrode of a dual frequency, fixed gap, capacitively-coupled parallel plate commercial etch system. We studied the relationship between the etch performance of NF3/Ar/He plasma and the discharge complex impedance and dissipated power. A 300mm diameter test wafer substrate, with ~3-5% of its surface area occupied by vias patterned into a 360nm thick carbon-doped oxide (CDO) deposited on top of a 300nm silicon carbide (SiC) layer, was utilized for etch rate characterization. Both the CDO and SiC films were exposed to the plasma and etched at the same time, mimicking the process of SiC barrier etch used at the end of a dual damascene patterning process flow. We varied the NF3 flow rate form 0 to 18% of the total flow over a pressure range from 10mT to 150mT. Under dual frequency excitation, where 400Watts 60MHz and 50 Watts13.56MHz were applied to the top and bottom electrodes, respectively, the discharge complex impedance changed drastically over the tested pressure range. Below 40mT, the discharge is characterized by low impedance (~10-20 ohm). As the pressure increases, the impedance increases and reaches an asymptote at the 20-25 ohm range. This general trend was not observed under the 13.56MHz single frequency excitation mode, where a monotonic decrease in impedance with increasing pressure was observed regardless of diluents. We propose a model, similar to Langan's et al.,@footnote 1@ suggesting that the dominant role of the diluent in NF3 plasmas is to control the electronegativity of the discharge, and thus to control real power dissipation. @FootnoteText@@footnote 1@J. Langan, S. Beck, B. Felker and S. Rynders, J. Appl. Phys. 79(8), pp.3886, 15 April 1996.

3:20pm **PS1-MoA5 Polymer Management in Dielectric Etch***, **E.A. Hudson**, A. Marakhtanov, K. Takeshita,* Lam Research Corp. **INVITED**

Etching of dielectric films for microelectronics requires processes which provide control of feature profiles and high selectivity to mask and stop layer films. For most dielectric films, especially Si-containing materials, plasma etch processes tend to deposit fluorocarbon or hydrofluorocarbon films. These polymeric films play many essential roles, acting to passivate feature sidewalls, to control critical dimensions and profile angles, to reduce mask loss, to minimize corner faceting, and/or to protect underlayers. But polymer deposition on reactor surfaces can lead to difficulties in maintaining stable reactor conditions. This paper focuses on several critical areas in dielectric etch processing where understanding and managing the behavior of deposited polymer is crucial. One focus is the effect of polymer upon microscopic structures. For example, low-k dielectric films tend to be modified by photoresist removal processes. Protective sidewall films have shown the capability to limit strip-induced damage. In another example, fluorocarbon films prepared under simulated conditions for sidewall vs top surfaces have shown different properties. These differences can influence final etch profiles. Another focus is the behavior of polymer on reactor surfaces. Multi-step in-situ processing has become a standard production method for reducing cost and cycle time. To maintain a stable process, it is important to understand how the chamber condition evolves during the sequential etch steps, and to minimize the interaction between these steps. Several process and plasma parameters influence the measured deposition rate of polymer on reactor surfaces. For transitions from a polymerizing step to a step which can etch polymer, the plasma conditions and process results may be influenced by the removal of residual chamber polymer. Time-resolved plasma measurements show the extent of this step-to-step chamber memory effect, and how it can be minimized.

4:00pm **PS1-MoA7 Polymer Management in Advance Dielectric Etch Applications***, **G.A. Delgadino**, D. Buchberger, Y. Zhou, Y. Xiao,* Applied Materials, Inc.

Historically, dielectric etch has rely on polymer deposition to achieve desire selectivity to photoresist and barrier film. As features size shrinks, softer shorter wavelengths photoresist are required. In particular, 193nm PR is not only thinner but also more prone to form veils and striations. Heavy polymer deposition is usually used to protect Photoresist and to minimize pinhole formation and striations. Unfortunately fluorocarbon deposited on the wafer and the chamber is released during insitu ashing attacking the barrier layer and sidewall. In this paper we describe the development of a polymer rich recipe that greatly protects photoresist resulting in no top view striation. Minimal barrier loss can be achieved by depositing a thin polymer film over the barrier minimizing barrier loss during ashing. Polymer also deposits in undesired places like the back side of the wafer. Small gaps allow polymer precursors to diffuse in but prevent the ashing plasma to rich the same spots. This deposited polymer might flake during other wafer processing steps reducing yield,@footnote 1@ or might just contaminate other process equipment like the PVD preclean chamber increasing frequency of maintenance. In this work we evaluate intra-chamber and intra-system solutions compatible with low k porous films, to minimize yield loss related to such undesired deposition. @FootnoteText@ @footnote 1@ T. Dalton et. al. AVS 2004.

4:20pm **PS1-MoA8 Analysis and Impact of F Penetration into low-k Dielectrics during Plasma Etch***, R. Augur,* ***C. Labelle,*** Advanced Micro Devices Inc.*; C. Parks, S. Mehta, N.C.M. Fuller,* IBM Corporation

The semiconductor industry's move towards incorporating porous low-k dielectrics in future technology generations raises many questions about the thermal, mechanical, and chemical interactions between porous dielectrics and the different environments they will encounter during integration. This paper reports detailed analysis of F penetration into porous and dense SiCOH-based low-k dielectrics, introduced during plasma etch. SIMS depth profiling was used to compare the concentration of F in etched and non-etched regions. For porous materials, the F concentration was found to be approximately 5 times higher in via-etched regions, and lateral penetration occurred throughout the thickness of 300nm films. Profiles were similar for spin-on (SOD) and chemical vapor deposited (CVD) films, even though the pore-size distribution and average pore size were different. Furthermore, profiles from dense CVD low-k films were also similar to those from porous films, even though the etch conditions were very different for the two cases. These results suggest porosity does not play a major role in F diffusion into SiCOH-based low-k materials. Profiles from the bottom of wide trenches were also similar to via-etched cases: high F concentration compared to non-etched regions, and penetration to 100nm below the trench bottom. The results of this study show F can be incorporated in low-k dielectric films during etch, and not completely removed during the subsequent resist strip. The F can interact with the strip chemistry to significantly etch the ultra-low-k material, and may cause reliability problems later.

4:40pm **PS1-MoA9 Effect of Species Density and Ion Scattering During Ashing on Ultra Low-@kappa@ Inter-Level Dielectric Films***,* ***M.A. Worsley***[1], Stanford University*; S.F. Bent,* Stanford University, US*; N.C.M. Fuller, J. Doyle, M. Rothwell,* IBM TJ Watson Research Center*; T.L. Tai,* IBM Microelectronics Division*; T.J. Dalton,* IBM TJ Watson Research Center

The challenge of integrating ultra low-@kappa@ inter-level dielectric (ILD) materials in dual damascene integration schemes continues be a key issue in the microelectronics industry. For the 45 nm technology node and beyond, the ITRS roadmap predicts the need for porous organosilicate glass (OSG) materials. It has been shown that these porous OSG materials are even more susceptible to modification by photoresist ash plasmas than dense OSG films. Therefore, a more detailed understanding of the plasma characteristics that mitigate this modification is critical for successful integration of ultra low-@kappa@ ILDs in current integration schemes. Previous work by these authors has revealed several factors that influence modification using various techniques focused on analysis of the modified ILD. The present work combines that material analysis of the modified ILD with characterization of some key parameters in the plasma and at the plasma-surface interface. In this study, optical emission (OE) actinometry is used to measure the absolute densities of reactive radical species, and modeling of various plasma parameters (sheath thickness and positive ion mean free path) is used to estimate the significance of ion scattering in several ashing plasmas. Patterned structures in a porous OSG are ashed in conditions identical to that characterized and then analyzed using angle-resolved x-ray photoelectron spectroscopy (ARXPS). Data from the OE actinometry and modeling are combined with the ARXPS data to gain further insight into the mechanism by which modification of the OSG occurs in a patterned structure. Relevant results will be presented.

5:00pm **PS1-MoA10 Behaviors of Fluorocarbon Radical Temperature in Ar/N@sub 2@/C@sub 4@F@sub 8@ low-k Etching Plasma***,* ***M. Nagai****, M. Hori,* Nagoya University, Japan

Fluorocarbon plasma has been used for various fields of material processing. Recently, low dielectric (low-k) films are used for interlayer dielectrics in ULSI. The etchings of low-k films such as SiOCH have been developed with Ar/N@sub 2@/C@sub 4@F@sub 8@ plasma. One of the most serious problems of low-k films etching is a line edge roughness of resists, which is considered to be closely related with the behaviour of the radical. Recently, several techniques have been employed to measure fluorocarbon plasmas. Optical emission spectroscopy (OES) is a powerful tool to measure the radical temperatures because it does not require complicated system such as a laser. In this study, we investigated behaviors of radicals in 60 MHz capacitively coupled plasma (CCP) using Ar/N@sub 2@/C@sub 4@F@sub 8@ gases. OES was applied to measure rotational temperatures of CF radical and neutral molecule in the excited state. The N@sub 2@ rotational temperature was used for the neutral gas temperature in plasma. Infrared diode laser absorption spectroscopy (IRLAS) was applied to measure rotational temperatures and densities in the ground state. The CF rotational temperature was increased from 290 K to 430 K with increasing N@sub 2@ flow rate in Ar/N@sub 2@/C@sub 4@F@sub 8@ plasma. The rotational temperature using OES was equilibrium with the rotational temperature using IRLAS. It was found therefore that the rotational temperatures in the excited state were equilibrium with the rotational temperatures in the ground state. CF radical density was decreased from 1.5 x 10 @super 12@ cm@super -3@ to 0.6 x 10@super 12@ cm@super -3@, and F atom density was increased with increasing N@sub 2@ gas flow rate. The decrease of the CF radical density was due to the recombination with CF radical and N atom. One of the mechanisms of the increase of the CF rotational temperature was due to Franck-Condon effect with the increase of the electron temperature with N@sub 2@ addition.

Plasma Science and Technology
Room 304 - Session PS2-MoA

Silicon Etching

Moderator: D. Leonhardt, US Naval Research Laboratory

2:00pm **PS2-MoA1 Advanced Gate Stack Etch Modeling for 65 nm Node***,* ***P.J. Stout****, M. Shroff, T. Stephens, J.E. Vasek, O.O. Adetutu, S. Rauf, P. Ventzek,* Freescale Semiconductor, Inc.

A reactor/feature modeling approach has been applied to etching an advanced gate stack. The reactor model is HPEM (developed at the University of Illinois) and the feature model is Papaya (developed at Freescale). Papaya is a 2D/3D Monte Carlo based feature scale model. The reactor model supplies Papaya with the identity, flux rate, angular distribution, and energy distribution of specie incident on the feature surface. Papaya has also been coupled to lithography models to obtain the initial resist profile used as a mask during the etch process. The gate stack consists of polysilicon, an anti-reflective coating, and a hard mask. Discussed will be the 3D feature modeling of the plasma etch steps required to etch through the gate stack. The cummulative effect of the gate etch steps is studied. The influence each etch step has on subsequent steps will be explored. The photoresist profile and feature proximity effects on the final polysilicon profile will also be discussed.

2:20pm **PS2-MoA2 Investigation of Gate Oxide Behavior during Highly Selective Poly-Si Gate Etching for Triple Gate Transistors***,* ***D. Kim****, H.S. Lee, S.J. Park, Y.J. Jee, K.K. Chi, C.J. Kang, H.K. Cho, J.T. Moon,* Samsung Electronics, South Korea

Triple gate transistor, or FinFET, is one of the most promising candidates for the next CMOS technology. FinFETs have better capability for higher transistor current and better controllability for the short channel effect, especially for sub 50nm ULSI devices. However, focusing on the fabrication aspects, the structure of FinFET has difficulties to overcome, which are inherently originated from using the fin-shaped active structure: (1) The thin gate oxide should be able to stand for the large amount of gate poly-Si etching not to leave any residues on the sidewalls and the bottom area of the 3-dimensional fin structure. (2) We should also overcome the undercut or tapering of the gate profile on the top and sidewall of the active area, which also originate from the 3-dimensional fin structure. These directly affect transistor characteristics such as threshold voltage distribution. In this work, we report detailed analyses on highly selective poly-Si gate etching for a FinFET. Since poly-Si etching should be carried out to the bottom area of the fin with G-ox exposed to the etch environment, high etch selectivity to G-ox is required. From this point of view, we tried to fully figure out how initial G-ox is affected by polymer deposition on G-ox, etching of G-ox itself, and plasma oxidation of silicon beneath the G-ox, which compete with one another during the gate etching. Transmission Electron Microscope (TEM) analysis, G-ox wet etch rate measurement, and measurement of electrical characteristics such as density of interface trap, charge density, leakage current were implemented. Based on the above investigations, plasma oxidation is considered to play an important role in gate etching with thin G-ox. It is also shown that the silicon-containing byproduct during gate etching is indispensable for polymer generation.

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[1] **PSTD Coburn-Winters Student Award Finalist**

2:40pm **PS2-MoA3 Silicon Etching Beyond the 90nm Technology Node: the Need for Total Parameter Flexibility***, **A.M. Paterson**, T. Panagopoulos, T.J. Kropewnicki, V. Todorow, A. Matyushkin, B. Hatcher, S. Pamarthy, N. Gani, A. Khan, S. Deshmukh, M. Shen, T. Lill, J.P. Holland,* Applied Materials **INVITED**

As CMOS technology node sizes push further into the nano-scale domain (sub 100nm) it has initiated new challenges for the silicon etching of logic and DRAM structures. In order to keep abreast of Moore's Law, new gate materials, geometries and architectures are currently being explored by IC manufactures with the intent of driving the node size to 32 nm by the end of this decade. Such device scaling brings new demands to wafer etch suppliers, with even more stringent etch requirements expected. At present, 90 nm technology is the smallest node in volume production, with the gate lengths being approximately 65 nm and CD bias requirements of 4 nm 3s over the entire 300 mm wafer, 3 mm edge exclusion. CD bias control is of paramount importance as it directly correlates to processor speed and cost. For smaller nodes the combination of resist trimming and curing (to prevent Line Edge Roughness (LER)) and process parameter flexibility become even more crucial in controlling the gate CD bias. This presentation will focus on the research and development work undertaken at Applied Materials to produce novel silicon etch equipment that will enable IC manufactures to obtain their goals for continued node size reduction. Experimental and theoretical work will be discussed showing the many novel features of an advanced 300 mm Applied Centura® DPS® process chamber for sub-65 nm gate, Shallow Trench Isolation (STI) and capacitor etches. This chamber has been designed to produce precise resist trimming / curing with total process step parameter flexibility allowing CD bias control of less than 3 nm 3s, 2 mm edge exclusion, for sub-65 nm technologies.

3:20pm **PS2-MoA5 Silicon Gate Etching using Amorphous Carbon Hard Mask***, **F. Lazzarino**,* CNRS/LTM, France*; P. Gouraud,* STMicroelectronics, France*; T. Chevolleau, B. Pelissier, G. Cunge, L. Vallier, O. Joubert,* CNRS/LTM, France*; T. Lill,* Applied Materials

Nowadays, the development of new integrated circuit generations requires the introduction of new materials. Among them, the amorphous carbon (a-C) is a promising candidate as a hard mask for gate etching processes due to its high selectivity to silicon (6:1). Moreover, since the conventional photolithography is not able to achieve resist linewidth lower than 80 nm, the trimming of a-C can be used as a new strategy to obtain sub-30 nm gate length. In this paper, an etch integration scheme using a-C hard mask is evaluated on 300 mm wafers and fully characterized for undoped, n-doped and p-doped wafers. The gate stack is composed of 1.2 nm SiON gate oxide, 100 nm polysilicon film, 100 nm PECVD amorphous carbon, 20 nm dielectric anti-reflective coating (DARC). The wafers are patterned with a 193 nm lithography and etched in an industrial inductively coupled plasma reactor. The resist trimming combined with the a-C trimming is investigated using different types of halogen chemistries containing oxygen (HBr/O@sub 2@, Cl@sub 2@/O@sub 2@,...) which allow to obtain sub-30 nm gate structures. The polysilicon gate is etched in conventional HBr/Cl@sub 2@/O@sub 2@ chemistries and the impact of the plasma parameters on the etch rates and both undoped and doped (n and p) gate profile is evaluated. Futhermore, chemical topography analyses by quasi in-situ X-ray Photoelectron Spectroscopy (XPS) are performed in order to correlate the etch profiles with the chemical composition of the passivation layers deposited on the sidewalls of the polysilicon gate.

3:40pm **PS2-MoA6 Atomic Scale Etching of Poly-Si in Inductively Coupled Ar and He Plasmas***, J.-H. Min,* Seoul National University, Korea*; S.H. Moon,* Seoul National University, Korea, South Korea*; Y.W. Kim,* FOI Korea Corporation, Korea*; C.B. Shin, **C.-K. Kim**,* Ajou University, Korea

For fabrication of novel Si-based devices, device structures with a high aspect ratio are increasingly required. The reactive ion etching is widely used for defining fine features, but energetic ions generated in a plasma are known to cause serious radiation damages. In a low-energy ion system, isotropic chemical reactions caused by neutrals become predominant and the deterioration of the pattern definition will occur. Therefore, a new concept of directional etching with minimum reaction energy is needed. In this work, atomic scale etching of poly-Si was performed by using a cyclic process of etchant adsorption and ion beam irradiation. This process is the same as the so-called atomic layer etching of single crystalline Si. Cl@sub 2@ was used as an etchant gas, and Ar or He ions generated in an inductively coupled plasma was used as an ion beam. The self-limiting characteristic of the etch rate with respect to the duration of ion irradiation for poly-Si etching was significantly different from that for single crystalline Si etching. That is, as the duration of the ion irradiation increased, the poly-Si etch rate was initially increased and converged to about 0.6Å/cycle and then rapidly increased, eventually showing a characteristic S curve. When He ions were used as an ion beam, the bias voltage region where the etch rates were smaller than the sputtering rates was observed, which was in contrast to the case where Ar ions were used as an ion beam. It is believed that this is because the size and mass of He ions are much smaller than those of chlorine atoms adsorbed on the poly-Si surface and therefore the chlorine atoms effectively prevent the poly-Si layer from being sputtered by the He ions.

4:00pm **PS2-MoA7 Spectroscopic and Real-Time Study of Ar@sup +@ and XeF@sub 2@ Etching of Si(100) by Second Harmonic Generation***, **A.A.E. Stevens**[1], P.M. Gevers, J.J.H. Gielis, M.C.M. Van De Sanden,* Eindhoven University of Technology, The Netherlands*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands*; H.C.W. Beijerinck,* Eindhoven University of Technology, The Netherlands

To gain new insights into the fundamental processes occurring at surfaces during plasma etching, Second Harmonic Generation (SHG) has been employed to study the etching of Si(100) in an Ar@sup +@/XeF@sub 2@ beam etching experiment. SHG by a medium is only allowed when inversion symmetry of the medium is broken and is therefore possibly extremely sensitive to surfaces and interfaces. Using a Ti:Sapphire laser in the 710 to 920 nm wavelength range the strain-induced resonance of Si-Si bonds (2.70-3.44 eV) has been probed before, during and after etching by Ar@sup +@ ions and XeF@sub 2@. Low-energy (20-2000 eV) ions impinging onto the Si(100) create a damaged, amorphized Si layer, which leads to an enormous increase in the SH signal within less than 1 ML Ar@sup +@ dose, and broadening of the resonance, indicative for an amorphous medium. XeF@sub 2@ passivation of the surface after the ions are switched off reveals that the signal originates not only from the surface but also from a buried interface between the damaged and crystalline silicon. At the switch-on of the XeF@sub 2@ after the ion bombardment an immediate increase of the SH signal (at 3.42 eV) can be observed showing an instant reaction of F with the highly reactive amorphous silicon surface. For XeF@sub 2@ etching of Si(100) two separate spectral features in the SH signal can be distinguished. After the XeF@sub 2@ is switched off, the spectral features change, indicating a reconstruction of the reaction layer. Furthermore, dosing a hydrogen terminated surface with XeF@sub 2@ shows an increase in the SH signal over the full spectral range before the actual etching begins as a result of the initial binding of F to Si. These and other observations will be discussed, which have led to some surprising new insights in the etch mechanism of Ar@sup +@ and XeF@sub 2@ of Si(100), showing that SHG is a promising, powerful diagnostic tool for surface sensitive studies of etch mechanisms.

4:20pm **PS2-MoA8 Optimization of Cryogenic Processes with Plasma Diagnostics***, **T. Tillocher**, R. Dussart, X. Mellhaoui, P. Lefaucheux, N. Mekkakia Maaza,* GREMI - Université d'Orléans, France*; M. Boufnichel,* ST Microlectronics*; L.J. Overzet,* University of Texas at Dallas*; P. Ranson,* GREMI - Université d'Orléans, France

The so-called cryogenic process is a good alternative to the Bosch process for the etching of high aspect ratio structures. Indeed, etching and passivation occur simultaneously and anisotropic profiles result from a balance between these two mechanisms. Consequently, high etch rates can be reached with relatively smooth profiles. This equilibrium is put into evidence with mass spectrometry and optical spectroscopy on maskless silicon wafers : an oxidation threshold appears from one oxygen percentage in the SF@sub 6@/O@sub 2@ plasma where the etch rate drops. In such a case an overpassivation regime is reached, which strongly reduces the etching. We have shown that this threshold depends on the substrate temperature, the source power and the chuck self-bias : a lower temperature involves a higher sticking coefficient of oxygen on silicon and a higher energy transmitted to the wafer by the ions can prevent the formation of the layer. We think that these results, which can be characterized with a simple model, can also be correlated to the etching of high aspect ratio patterns. Indeed, the interaction between the surface and the radicals is quite similar on a bulk silicon wafer and on the sidewalls of the patterns. This appears to be a way to find the optimum oxygen flow. Plasma diagnostics, such as mass spectrometry, optical emission spectroscopy and Langmuir probe can also be used to optimize the other plasma parameters, especially the SF@sub 6@ flow and the source power. Finally, we will present performances which can be reached with optimized processes in the case of holes etching for the drilling of 400 µm thick silicon wafers.

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[1] **PSTD Coburn-Winters Student Award Finalist**

4:40pm **PS2-MoA9 The Role of the Reaction Products in the Silicon Etching Cryogenic Process***, **R. Dussart**, X. Mellhaoui,* GREMI - Universit@aa e@ d'Orleans, France*; T. Tillocher,* GREMI, France*; P. Lefaucheux, N. Mekkakia Maaza,* GREMI - Universit@aa e@ d'Orleans, France*; M. Boufnichel,* ST Microelectronics, France*; L.J. Overzet,* Univ. of Texas at Dallas*; P. Ranson,* GREMI - Universit@aa e@ d'Orleans, France

The cryogenic process of silicon deep etching can be used in MEMS and power microelectronic component fabrication. In this process, a SF6/O2 plasma is used to etch high aspect ratio silicon microstructures. The bottom of the structure, which is submitted to ion bombardment, is etched while lateral etching is inhibited by the formation of a SiOxFy passivation layer. This layer, which only appears at low temperature and with oxygen, is continuously deposited on the microstructure sidewalls during the etching process. The formation of this passivation layer is not well characterized. It mostly desorbs when the wafer is warmed up to ambient temperature. In particular, the role of SiF4 (the main etching product) is not well understood. Experiments with SiF4/O2 and SF6/O2 plasmas were carried out to investigate the formation of the passivation layer. Mass spectrometry, profile characterization by SEM and ellipsometry measurements were carried out to better understand the role of SiF4 in the passivation layer formation in the cryogenic process.

5:00pm **PS2-MoA10 The Characterization of Silicon Trench Etching in a High Density Reactor Using Self-Excited Electron Resonance Spectroscopy (SEERS)***, **F.C. Session**,* Fairchid Semiconductor, US

The development and characterization of a medium depth Si trench process for power IC applications, was performed utilizing Self-Excited Electron Resonance Spectroscopy (SEERS). SEERS provides volume averaged plasma parameters such as electron collision frequency, electron density and sheath width by monitoring the non-linearity of the space charge sheath at the electrode. Several etch chemistries were investigated including SF@sub 6@/ O@sub 2@, Cl@sub 2@/ O@sub 2@, HBr/ O@sub 2@, HBr/SF@sub 6@/O@sub 2@ and Cl@sub 2@/SF@sub 6@/O@sub 2@ and their effect on etch rate and sidewall profile. Pressure appears to be the overwhelming parameter in terms of profile and has a large effect on the electron collision rate and electron heating mechanisms. The study of pressure effects on electron temperatures and electron collision rates have been performed@footnote 1@ but these parameters have yet to be correlated to the actual etch performance and trench morphology. This study looks at these relationships and their effects on the optimized trench process.

Advanced Surface Engineering
Room 201 - Session SE-MoA

MAX Phases: Nanolaminates and Nanomechanical Measurements

Moderator: D. Gall, Rensselear Polytechnic Institute

2:00pm **SE-MoA1 The MAX Phases: Ductile, Machinable Ternary Carbides and Nitrides***, **M.W. Barsoum**,* Drexel University **INVITED**

With over 100 refereed publications and 8 patents in the past 8 years we have made tremendous progress in understanding the properties of a class of layered, hexagonal ternary carbides and nitrides with the general formula: M@subN+1@AX@sub n@ (MAX), where n = 1 to 3, M is an early transition metal, A is an A-group element and X is C or N. The MAX phases combine some of the best attributes of metals and ceramics. Like metals, they are electrically and thermally conductive, readily machinable, not susceptible to thermal shock, plastic at high temperatures, and exceptionally damage tolerant. Like ceramics, some are elastically rigid, lightweight, and maintain their strength at high temperatures. Ti@sub 3@SiC@sub 2@ is also creep, fatigue and oxidation resistant. Furthermore, basal planes of Ti@sub 3@SiC@sub 2@ possess very low friction coefficients (3x10@super -2@) that are quite robust vis-a-vis exposure to the atmosphere. Two characteristics distinguish these phases from other layered solids: i) the metallic-like nature of the bonding, and ii) they deform by a unique combination of kink and shear band formation resulting from the glide of basal-plane dislocations. Polycrystalline Ti@sub 3@SiC@sub 2@ cylinders can be repeatedly compressed at room temperature, up to 1 GPa. The stress-strain curves outline fully reversible, reproducible closed loops whose size and shape depend on grain size, but not strain rate. The energy dissipated per cycle is of the order of 1 MJ/m@super 3@. At the grain level we have shown that it is possible to nanoindent grains of Ti@sub 3@SiC@sub 2@ with up to 10 GPa, dissipate roughly 25 % of the mechanical energy and not be able to find any trace of the indentation. Both phenomena are attributed to the formation and annihilation of incipient kink bands. The technological implications of having these naturally nanolayered materials will be discussed.

2:40pm **SE-MoA3 Alternating Covalent-Ionic and Metallic Bonding in Nanolaminated Cubic Perovskites***, **D. Music**, J.M. Schneider,* RWTH Aachen, Germany

Using ab initio calculations, we have studied 35 cubic perovskites of RM@sub 3@X stoichiometry, where R and M are metals and X is a 2p nonmetal. In this structure (space group Pm-3m, prototype CaTiO@sub 3@), R atoms fill primitive cubic sites, M atoms are located at face centered cubic positions, and X is placed at body centered cubic Bravais nodes. We show that the coupling between M-R and M-X layers in RM@sub 3@X can be switched from predominantly covalent-ionic to metallic in character by varying the population of the M and R d-shells. As the X 2p population increases, the bulk modulus decreases, which can be understood by changes in bonding character from more covalent to more ionic due to splitting in density of states. We will also discuss transport properties obtained from phonon calculations. Based on the electron density distribution resemblance to the so-called MAX phases, it is reasonable to assume that alternating covalent-ionic and metallic bonding in these compounds may give rise to similar properties as observed for MAX phases.

3:00pm **SE-MoA4 Observation of the Growth and Microstructural Development of MAX Phase Ti@sub 2@AlN Thin Films during Magnetron Sputtering using Synchrotron Radiation***, **N. Schell**, M. Beckers, R.M.S. Martins, A. Mücklich, W. Möller,* Forschungszentrum Rossendorf, Germany

The heteroepitaxial growth of MAX phase Ti@sub 2@AlN (M@sub n+1@AX@sub n@ with M = Ti, A = Al, X = N and n = 1) on single crystal substrates MgO(001) and MgO(111), deposited by reactive magnetron co-sputtering from Ti and Al targets in an Ar/N@sub 2@ atmosphere at a temperature of 690°C, has been studied in situ. Using real-time specular x-ray reflectivity, layer-by-layer growth first of an approximately 10 nm thick epitaxial B1-cubic Ti@sub 0.63@Al@sub 0.37@N seed layer, then, after changing the deposition parameters, of the MAX phase itself was observed, with an increased surface-roughening on MgO(001) substrate. Using off-plane Bragg-Brentano x-ray scattering, the heteroepitaxial growth of Ti@sub 2@AlN to the underlying seed-layer as well as MgO was established with lattice parameters of c = 1.3463 nm and a = 0.2976 nm. From ex-situ pole figures at a laboratory source the epitaxial relationship between film and substrate lattice was determined to be MgO {111} // Ti@sub 2@AlN {1012;¯}[1;¯21;¯0]regardless of choice of substrate orientation during deposition, e.g. a non-basal plane epitaxial growth of the Ti@sub 2@AlN thin films along MgO directions, leading to a threefold grain orientation as also seen in cross-sectional transmission electron microscopy. In temperature dependent four-probe measurements at room temperature a specific resistivity of 37 µ@ohm@cm has been derived.

3:20pm **SE-MoA5 The Materials Science of MAX Phase Thin Films***, **L. Hultman**,* Linköping University, Sweden **INVITED**

This presentation is a review of the materials research on M@sub n+1@AX@sub n@ (n=1 to 3) phase thin films. We have deposited epitaxial films from the Ti-Si-C, Ti-Ge-C, and Ti-Sn-C as well as Ti-Al-N systems on Al@sub 2@O@sub 3@(0001) or MgO(111) substrates at temperatures of 700-1000C employing DC magnetron sputtering. This was done using mainly growth from elemental sources, but also demonstrating single source deposition from compound targets. We report single-crystal growth of the previously known phases Ti@sub 3@SiC@sub 2@, Ti@sub 3@GeC@sub 2@, Ti@sub 2@GeC, Ti@sub 2@SnC and Ti@sub 2@AlN, and the discoveries of two phases Ti@sub 4@SiC@sub 3@ and Ti@sub 4@GeC@sub 3@ as well as intergrown structures of stoichiometries Ti@sub 5@A@sub 2@C@sub 3@ and Ti@sub 7@A@sub 2@C@sub 5@ in the Si and Ge systems. Characterization studies will be reported using XRD, TEM, four-point (resistivity) probe, and nanoindentation. Comparison will also be made with the phase composition in nanocomposite M-A-X films forming during deposition at reduced temperature.

4:00pm **SE-MoA7 The Promise of High Power Pulsed Magnetron Sputtering (HPPMS)***, **W.D. Sproul**,* Reactive Sputtering Consulting **INVITED**

High power pulsed magnetron sputtering (HPPMS) applies a very large power pulse to the target in a short period of time. Typical power densities are on the order of 1,000 to 3,000 W cm@super -2@ with pulse durations of 100-150 µsec. This power density is about 100 times the typical power densities used in conventional sputtering. Depending on the size of the sputtering target, the peak power can reach the megawatt range. The very interesting feature of HPPMS is that there is a high degree of ionization of the sputtered species due to electron impact ionization, and most of the ionized species are singularly ionized although there are reports of small amounts of multiply ionized species of the target material. These ionized species can be used to improve the structure and properties of the deposited film, and the ionized species will follow field lines to a biased substrate producing a dense film in side wall features as has been demonstrated by Alami et al.@footnote 1@ In many respects HPPMS is very much like the cathodic are process where there is a very high degree of ionization of the evaporant, but unlike the arc process there are few if no droplets produced in the process. HPPMS has been used for reactive sputtering of conducting materials such as chromium nitride, and it has also been used for the reactive sputter deposition of the oxides of Al, Ta, and Ti. The one disadvantage of the HPPMS process that has come to light so far is that its deposition rate is only 25-30% of the rate for an equivalent amount of power used during conventional DC sputtering. A model by Christie@footnote 2@ has been developed to explain this loss of rate for the HPPMS process, and the model provides insights that hopefully will bring a solution to this loss of rate issue. In this talk, the current state of the art for HPPMS will be reviewed with an eye toward the future to see where HPPMS can be used to benefit the thin film community. @FootnoteText@@footnote 1@J. Alami, P. O. @Ao@. Persson, D. Music, J. T. Gudmundsson, J. Bohlmark, and U. Helmersson, J. Vac. Sci. Technol. A 23, 278 (2005). @footnote 2@D. J. Christie, J. Vac. Sci. Technol. A 23, 330 (2005).

4:40pm **SE-MoA9 Towards Large Area Deposition of Cr@sub 2@AlC on Steel***, C. Walter, D.P. Sigumonrong,* RWTH Aachen, Germany*; T. El-Raghy,* 3-One-2 LLC*; **J.M. Schneider**,* RWTH Aachen, Germany

Cr@sub 2@AlC belongs to the MAX phases, which are promising materials for protective coatings on steel due to their unique combination of properties like corrosion and oxidation resistance and damage tolerance. Here the deposition by magnetron sputtering of a Cr-Al-C compound target was investigated varying the substrate temperature and the substrate bias potential. It was found that the MAX phase structure is stable in a substrate temperature range between 850 and 450 °C. At lower substrate temperatures the structure of the film is X-ray amorphous. Varying the DC substrate bias potential between floating potential and 310 V, no significant influence on the film composition and structure was observed. A phase purity of more than 90 % MAX phase in the films was reached and the equilibrium volume measured by X-ray diffraction is in excellent agreement with our own ab initio calculations. The method discussed here may provide a pathway towards large area MAX phase deposition on steel.

Surface Science
Room 202 - Session SS1-MoA

Catalysis for the Hydrogen Economy

Moderator: G.B. Fisher, Delphi Research Labs

2:00pm **SS1-MoA1 In-situ CV and XPS Evaluation of Tungsten Carbides as Alternative Electrocatalysts***, **M.B. Zellner**, J.G. Chen,* University of Delaware

The purpose of this research is to examine the feasibility of using tungsten carbides (WC) and platinum modified tungsten carbides (Pt/WC) as direct methanol fuel cell (DMFC) and hydrogen fuel cell electrocatalysts. The motivation to study tungsten carbides stems from the fact that current fuel cells require the use of Pt or Pt/Ru anodes, which are expensive and easily poisoned by CO. The successful development of tungsten carbide electrodes as Pt/Ru substitutes can therefore positively influence the commercialization of DMFC and hydrogen fuel cell systems. Previously, reactions of CH@sub 3@OH, H@sub 2@O, H@sub 2@ and CO over single crystal and physical vapor deposited (PVD) thin film WC and Pt/WC surfaces have been studied with temperature-programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS). The results show that the carbide surfaces possess characteristics critical to application as fuel cell anodes. In particular, these surfaces are highly active toward the decomposition of CH@sub 3@OH and H@sub 2@O, and are able to desorb CO at relatively low temperatures. Recently, Pt-modified WC films along with PVD thin films of WC and W@sub 2@C have been tested for stability in an acidic environment and activity of methanol oxidation using an in-situ cyclic voltammetry (CV)/ X-ray Photoelectron Spectroscopy (XPS) test station. The tests show stability of WC to ~0.8 V wrt. NHE and a synergistic effect at monolayer Pt coverage, resulting in enhanced stability to ~1 V. Additionally, WC and Pt/WC surfaces show methanol O-H and C-H oxidation states, with the Pt/WC surface displaying greater methanol oxidation activity compared to WC or pure Pt foil.

2:20pm **SS1-MoA2 Development of a High Temperature Electrochemical Reactor with Differential Electrochemical Mass Spectrometry for Kinetic Rate Analysis of Methanol Oxidation***, **L.M. Roen**, E.M. Stuve,* University of Washington

Direct methanol fuel cells have nearly the same potential as hydrogen fuel cells, ~1.2 V, though practical implementation has been limited by the kinetics of methanol oxidation. A full Langmuir-Hinshelwood model was previously developed@footnote 1@ in order to ascertain the kinetic rates of each elementary step of methanol oxidation on platinum. The strongest criticism of this model was its neglect of partial oxidation products. In addition to the empirical approach, we are collaborating with a theoretical group using Density Functional Theory to predict the kinetics rates from first principles. Experimentally, we need 4 independent measurements at different temperatures to find the kinetic rates and activation energies. The experimental system was designed to meet several requirements: (1) clean electrolyte environment, (2) no loss of potential control between measurements, (3) heating control from room temperature to 95°C, (4) quantitative detection of CO@sub2@, and, (5) minimal time delay for detection of volatile species. We have successfully constructed an electrochemical microreactor with on-chip heating attached to a differential electrochemical mass spectrometer (DEMS) to meet these requirements. Expected results of the measurements are kinetic rate constants, activation energies, and Tafel slopes for five elementary steps in the methanol oxidation process; direct oxidation to CO@sub 2@, series oxidation of CO to CO@sub 2@, accumulation of the CO intermediate, incomplete oxidation of methanol, and adsorption of methanol; over temperature, potential, and concentration ranges of 22 - 100°C, 0.2 - 0.6 V@sub rhe@, and 0.01 - 5 M respectively. @FootnoteText@ @footnote 1@ S. Sriramulu, T.D. Jarvi, E.M. Stuve, Reaction mechanism and dynamics of methanol electrooxidation on platinum(111), J. Electroanal. Chem. 467 (1999) 132-142.

2:40pm **SS1-MoA3 Hydrogen Production and Conversion***, **I. Chorkendorff**,* Center for Individual Nanoparticle Functionality CINF, Denmark **INVITED**

On many levels there are strong efforts being made to find alternative ways of distributing energy in the future. Hydrogen is considered to be one of the more potential energy carriers. Since there is still a long way to go before we can produce hydrogen in sufficient amounts - and at competitive prices - directly from renewable energy sources, we will still have to rely on fossil fuels for many years to come. The fact that hydrogen, if combined with carbon dioxide sequestration, can be made from fossil fuel without contributing to the green house effect may be a route of soft transition. Today hydrogen is essentially produced by the so-called steam reforming process of natural gas. In a number of studies we have investigated the fundamental aspects of methane and CO conversion on Ni and Ru surfaces - especially with respect to the effect of structure. From studies of Nitrogen dissociation on Ru we have learned that the so-called B5 sites are simply dominating the reactivity. It is therefore also of interest to investigate how these types of defect sites may influence other reactions - for example those related to the hydrogen production, such as the steam reforming process and its reverse reaction: the methanization reaction. Non-conventional production and conversion of hydrogen are also interesting, particularly because the extensive use of fuel cells will require developing new electrode materials that can replace the expensive and scarce Platinum. We will discuss different routes for development of new electrode materials, involving both screening of alloy materials under well defined conditions combining high pressure cells with conventional UHV equipment, but also biomimetric approaches. The latter involves materials inspired by the active co-factors of nitrogenase and hydrogenase enzymes for electrochemical hydrogen production.@footnote 1@@FootnoteText@ @footnote 1@B. Hinnemann, P. G. Moses, J. Bonde, I. Chorkendorff & J. K. NÃ¸rskov, Accepted JACS (2005).

3:20pm **SS1-MoA5 The Electronic Structure Effect in Heterogenous Catalysis***, **A. Nilsson**,* Stanford University*; L.G.M. Pettersson,* Stockholm University, Sweden*; B. Hammer,* University of Arhus, Denmark*; T. Bligaard, C.H. Christensen, J. Norskov,* Technical University of Denmark

Transition metals are used extensively as catalysts and the variation in the catalytic activity for a given reaction is determined largely by the differences in the strength of the adsorbate-surface interaction from one metal to the next. In the following presentation we will demonstrate how we can understand trends in adsorbate-surface interactions based on a particularly simple picture that was originally developed to describe the difference in reactivity for hydrogen dissociation on metal surfaces, the d-band center model.@footnote 1@ We will show that it applies quite generally and in particular we will show that it can be validated through an experimental determination of the electronic structure of both occupied and unoccupied adsorbate states in an atom specific way using x-ray emission spectroscopy (XES) and x-ray absorption spectroscopy (XAS) together with density functional theory calculations (DFT).@footnote 2@ It has been shown that the catalytic activity of different transition metals as catalysts for ammonia synthesis is given by the strength of the nitrogen-surface bond.@footnote 3@ We will show that XES, XAS and DFT studies of atomic nitrogen can probe details of the metal d induced adsorbate electronic structure that can be linked to the chemisorption bond strength. @FootnoteText@ @footnote 1@B. Hammer and J. K. Norskov, Nature 376, 238 (1995). @footnote 2@A. Nilsson and L. G. M. Pettersson, Surf. Sci. Reps. 55, 49 (2004). @footnote 3@A. Logadottir, T. H. Rod, J. K. Norskov, B. Hammer, S. Dahl and C. J. H. Jacobsen, J. Catal. 224, 206 (2001).

3:40pm **SS1-MoA6 Microcanonical Transition State Theory: Closing the "Nonequilibrium Gap" Between Surface Science, Catalysis, and Electronic Structure Theory**, ***I. Harrison,*** University of Virginia

Progress towards achieving a unified kinetic picture of surface reactions has been uneven when nonequilibrium surface science and thermal equilibrium catalysis experiments have been compared and contrasted with electronic structure theory (EST) calculations of transition state characteristics. A simple microcanonical unimolecular rate theory (MURT) model of gas-surface reactivity has been able to largely close this "nonequilibrium gap" for several activated dissociative chemisorption reactions [e.g., CH@sub 4@ on Ni(100), Pt(111), and Ir(111); SiH@sub 4@ on Si(100); H@sub 2@ on Cu(111)]. The MURT's ability to quantitatively predict and directly compare the results of disparate equilibrium and nonequilibrium experiments to one another and to the calculations of EST will be shown to open up some useful new opportunities to rigorously test and refine our understanding of reactive transition states and kinetics at surfaces.

4:00pm **SS1-MoA7 First Principles Study of Factors Controlling the Rate of Ammonia Decomposition on Ni and Pd Surfaces**, ***S. Stolbov,*** *T.S. Rahman,* Kansas State University

Using the plane wave pseudopotential method within the density functional theory with the generalized gradient approximation for exchange and correlation potential, we have calculated adsorption energies (Ead), diffusion barriers and the first dissociation barriers (E1) for NH3 on Ni(111), Pd(111), Ni(211), and Pd(211). While the top site is found to be preferred for NH3 adsorption on both Ni(111) and Pd(111), the calculated diffusion barrier is substantially higher for Pd(111) than for Ni(111). We also find that during the first dissociation step (NH3 => NH2 +H) on both surfaces NH2 moves from the top site to the nearest hollow site, while on the stepped surface (211) it moves from the initial top site at the step edge to the bridge site in the same step chain. H is found to occupy the hollow sites for all four surfaces. For the reaction on Ni(111), E1 is found to be 0.23 eV higher than Ead, while at the step of Ni(211), E1 and Ead are almost equal. This suggests that the molecule would rather desorb than dissociate on Ni(111), and dissociate on the stepped surface. On the other hand in the case of Pd surfaces, we find that the dissociation barrier is much higher than Ead, even for the stepped surface. This may explain why ammonia decomposition rate on Pd is much lower than that on Ni.

4:20pm **SS1-MoA8 Water Chemistry on Cu(110): from Ultra High Vaccum to Ambient Conditions**, ***K. Andersson,*** Stanford University / Stockholm University, Sweden*; H. Bluhm, G. Ketteler,* Lawrence Berkeley National Laboratory*; H. Ogasawara, T. Schiros,* Stanford Synchrotron Radiation Laboratory*; D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory*; A. Nilsson,* Stanford Synchrotron Radiation Laboratory

Probing the coverage and chemical speciation of molecules at surfaces are of fundamental interest in the fields of heterogeneous catalysis and molecular environmental science. We present in-situ studies of water adsorption on Cu(110) at pressures up to 1 Torr in the temperature range 270 - 470 K using synchrotron-based photoelectron spectroscopy. Partial coverages of atomic O, OH, and H@sub 2@O are reported under various conditions. We compare our results to those obtained under ultra high vacuum conditions where we have found a water dissociation onset at about 160 K with an activation barrier of 0.53-0.56 eV.@footnote 1@ @FootnoteText@ @footnote 1@ K. Andersson, A. Gómez, C. Glover, D. Nordlund, H. Öström, T. Schiros, O. Takahashi, H. Ogasawara, L.G.M. Pettersson, A. Nilsson, Surf. Sci. Lett., in press (2005).

4:40pm **SS1-MoA9 Hydrogen Interactions with Quasicrystalline Aln-; Pd-& n-; Mn Surfaces**, ***C.J. Jenks,*** *T.A. Lograsso,* Ames Laboratory, Iowa State University*; J. Whaley, R. Bastasz,* Sandia National Laboratories

The interaction of molecular and atomic deuterium with the fivefold surface of icosahedral (i-) Aln-Pdn-Mn using angular-resolved low-energy ion scattering under ultrahigh vacuum conditions will be discussed. i-Aln-Pdn-Mn is known to form a clean laterally-bulk-terminated surface after sputtering and annealing in excess of 800 K. Despite no two layers within a this material being identical, certain types of planes are favored, namely those that are Al-rich (> 77 atomic percent). The density of Al atoms on the clean surface of fivefold i-Aln-Pdn-Mn is about that of Al(111) and thus we compare our results to studies of molecular and atomic hydrogen on Al(111). We are able to confirm, using ion scattering of 2 keV neon ions and direct recoil measurements, previous thermal desorption studies that indicated that molecular deuterium does not dissociate on this surface. Molecular deuterium, likewise, does not dissociate on Al(111). Atomic hydrogen, however, we find readily adsorbs on both surfaces. On fivefold i-Aln-Pdn-Mn we find that atomic deuterium adsorbs on top of the surface and that it strongly attenuates the signals for Al, Pd and Mn along particular azimuthal directions. Based on this information we will discuss the deuterium adsorption geometry on i-Aln-Pdn-Mn and compare the results to those for Al(111). This work is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences under Contracts no. W-405-Eng-82 and DE-AC04-94AL85000.

5:00pm **SS1-MoA10 Detection of Nitric Oxide using Gold Nanoparticle Catalysts on WO@sub3@ Chemiresistive Sensors**, *A.L. Martin,* University of Maine*; J. Wang,* Bangor High School*; G. Bernhardt,* University of Maine*; M. Sander,* Inst. Materials Res. Eng., Singapore*; R.J. Lad, F.G. Amar,* ***B.G. Frederick,*** University of Maine

Detection of nitric oxide at parts-per-billion levels is important for environmental and medical applications. We have shown that NO can be detected on tungsten trioxide chemiresistive sensors if gold or silver nanoparticles are present. The sensitivity, dynamic range, and response time depend upon the metal coverage and particle size distribution. In the limit that NO to NO@sub2@ conversion and spillover/diffusion is fast compared to NO@sub2@ reaction, the mean field solution is consistent with the initial, linear dependence of sensor response on NO partial pressure. Changes in the gold nanoparticle particle size distribution were measured with high resolution SEM. We have modeled the adsorption and conversion of NO to NO@sub2@ on the metal catalyst, followed by spillover, diffusion and reaction of NO@sub2@ with oxygen vacancies on the WO@sub3@(001) surface using kinetic Monte Carlo simulations. The spatial inhomogeneity results in a non-linear sensitivity curve, which is consistent with sensor response after aggregation.

Surface Science
Room 203 - Session SS2-MoA
Oxide Surfaces Structure and Reactivity

Moderator: M.A. Langell, University of Nebraska-Lincoln

2:00pm **SS2-MoA1 Reconstrutions of the Polar Oxide Surface MgO(111)**, ***S.E. Chamberlain,*** *D.A. Human, X.F. Hu, H.C. Poon, D.K. Saldin, C.J. Hirschmugl,* University of Wisconsin-Milwaukee

Structures of polar oxide surfaces have been of great interest with several models proposed to compensate the "polar surface instability problem," including 1.) adsorption of foreign species, e.g., hydroxylated surface, 2.) surface faceting, 3.) metallization.@footnote 1@ MgO(111), the polar surface of a prototypical rocksalt structure, has been shown to maintain a 1x1 structure when annealed to low temperatures, and reconstruct when heated to higher temperatures,@footnote 2@ and thus represents an ideal system for detailed structural analysis. Detailed surface structures for the 1x1 and (@sr@3 x @sr@3)R30 ° reconstructions will be presented, which have recently been obtained with a novel, low-current LEED system. In good agreement with recent photoelectron diffraction and electronic structure calculations,@footnote 3@ the MgO(111)1x1 surface is mostly terminated with adsorbed OH groups mixed with a small percentage of O terminated patches with significant relaxation, and suggests that the hydroxylated surface is the compensation method of choice for MgO(111) 1x1. Results from the (@sr@3 x @sr@3)R30° reconstruction will be compared with several structures proposed in the literature.@footnote 2,4@ @FootnoteText@ @footnote 1@ C. Noguera, J. Phys.: Condens. Matter 12, R367 (2000)@footnote 2@ R. Plass, K. Egan, C. Collazo-Davila, D. Grozea, E. Landree, L. D. Marks, M. Gajdardziska-Josifovska, Phys. Rev.

Lett. 81 (1998) 4891.@footnote 3@ V. K. Lazarov, R. Plass, H-C. Poon, D. K. Saldin, M. Weinert, S. A. Chambers, and M. Gajdardziska-Josifovska Phys. Rev. B 71, 115434 (2005)@footnote 4@ Subramanian A, Marks LD, Warschkow O, Ellis DE, Phys. Rev. Lett. 92 (2004)200411.

2:20pm **SS2-MoA2 Effects of CH@sub 3@OH, H@sub 2@O and O@sub 2@ on Ultrathin Ordered Alumina Films under Non-UHV conditions: Hydrogen Bonding and Pressure Gaps***, M. Jain, F. Qin, M. Magtoto,* ***J. Kelber,*** University of North Texas

STM, AES and LEED have been used to probe the reactivities of ~ 7.5 Å thick, ordered Al@sub 2@O@sub 3@ films grown on Ni@sub 3@Al(110) and Ni@sub 3@Al(111) substrates for CH@sub 3@OH, H@sub 2@O and O@sub 2@ at intermediate pressures (10@super -8@ Torr - 10@super -1@ Torr) at room temperature. Results for H@sub 2@O show that at pressures above 10@super -4@ Torr, 300 K a surface reconstruction is initiated at defect sites which gradually leads to complete loss of long range order without formation of a UHV-stable hydroxide.@footnote 1@ The effect is pressure, rather than exposure-dependent, indicating a cooperative effect. Similar exposures to CH@sub 3@OH at > 10@super -4@ Torr, 300 K also induce a reorganization of the oxide film, though less severe than is observed for equivalent exposures of H@sub 2@O. STM constant current imaging at 2.0 V tip/sample bias of an Al2O3/Ni3Al(111) film after a total CH3OH exposure of 5.4 x 105 L at 10@super -4@ Torr, 300 K, reveals disordering of the oxide surface. Imaging at 0.1 V, and LEED however, reveals that the oxide/substrate interface still retains long-range order. C coverage remains < 0.05 monolayers at all exposures. Exposures of Al@sub 2@O@sub 3@/Ni@sub 3@Al(111) and Al@sub 2@O@sub 3@/Ni@sub 3@Al(110) to pure O@sub 2@ at pressures > 10@super -4@ Torr, 300 K result in no change to the film observable by AES, LEED or STM. No effect is observed for any of these gases at pressures < 10@super -7@ Torr, even for exposure times > 6 hours. These data indicate that intermolecular hydrogen bonding is important for inducing cooperative reactions at oxide surfaces and intermediate pressures.The data will be discussed with regards to issues of oxide stability and metal particle sintering during catalytic reactions. @FootnoteText@@footnote 1@F. Qin, N.P. Magtoto, J.A. Kelber, Surf. Sci. 565 (2004) L277. This work was supported by the Robert Welch Foundation under grant B-1356.

2:40pm **SS2-MoA3 Structural Characterisation and Reactivity of V@sub2@O@sub3@(0001) Thin Films***,* ***S. Guimond,*** *M.A. Haija, A. Uhl, H. Kuhlenbeck, H.J. Freund,* Fritz Haber Institute of the Max Planck Society, Germany

Vanadium oxides are used as catalysts for several oxidation reactions, including the selective oxidation of hydrocarbons and the oxidative dehydrogenation of alkanes to olefins. In spite of their importance, many questions about the molecular structure and the reaction mechanisms at their surfaces remain unanswered. For instance, a range of vanadium oxidation states exists (from 2+ to 5+) and it is often argued that lower oxidation states like V@sub2@O@sub3@ could take part in some of the reactions taking place at the surface of the V@sub2@O@sub5@-based catalysts. In the present work, we prepared well ordered V@sub2@O@sub3@(0001) thin films and studied their interaction with different molecules. The films were grown on Au(111) by evaporation of vanadium in a partial pressure of oxygen. Under typical UHV conditions, the films are terminated by vanadyl groups which are not part of the V@sub2@O@sub3@ bulk structure. As indicated by XPS and vibrational spectroscopy, the oxygen atoms contained in the V=O groups can be removed by electron irradiation, resulting in a surface terminated by metal atoms. This reduction process was followed with STM. The chemical activity of the two surfaces with respect to the adsorption of O@sub2@, H@sub2@O, CO@sub2@ and propane was investigated with XPS, IRAS and TDS. While the surface terminated by vanadyl groups was found to be chemically not very active, a rather high activity was observed for the V-terminated surface: O@sub2@ adsorption re-establishes the V=O groups via a charged precursor at low temperature, similar to the case of oxygen on Cr@sub2@O@sub3@(0001). After thermal desorption of an adsorbed CO@sub2@ layer, the surface is partially re-oxidized, meaning that part of the CO@sub2@ oxygen remains on the surface and forms vanadyl groups. Water dissociates on the surface, forming a layer of hydroxyl groups which is stable up to 500 K. Propane is partially transformed into propene, possibly via an oxygen-containing intermediate.

3:00pm **SS2-MoA4 The Multiple Roles of Oxygen in Organic Photo-oxidation on TiO2: Insights from Studies on a Model Photocatalyst Surface***,* ***M.A. Henderson,*** Pacific Northwest National Laboratory*; J.M. White, M.D. Robbins,* University of Texas at Austin*; H. Uetsuka,* Kanagawa Academy of Science and Technology, Japan*; H. Onishi,* Kobe University, Japan

The primary role that molecular oxygen has been viewed to play in organic photo-oxidation processes on high surface area TiO@sub 2@ photocatalysts has traditionally been restricted to that of an electron scavenger. However, some groups have proposed more direct involvement of O@sub 2@ in reactions with organics. Typical photocatalytic studies employ high surface area powders which are often difficult to characterize on the molecular scale. Results presented in this talk on a model TiO@sub 2@ photocatalyst, rutile TiO@sub 2@(110), provide more detailed information on the roles of O@sub 2@ and show that O@sub 2@ not only acts as an electron scavenger but also: is involved in thermal reactions with organics and OH groups, blocks organic adsorption sites, and competes with adsorbed organics for photo-generated holes. Results on the photo-oxidation of trimethyl acetate, isobutene and acetone will be used to illustrate these functions of O@sub 2@ during photocatalysis on TiO@sub 2@. Additionally, it will be shown that the function of oxygen oscillates through these different roles as a typical C@sub n@ hydrocarbon is oxidized to completion (i.e., to CO@sub 2@ and water) by sequential removal of C@sub 1@ units.

3:20pm **SS2-MoA5 Iron Oxide Thin Films as Supports for Model Catalytic Systems***,* ***S. Shaikhutdinov,*** Fritz-Haber Institute, Germany

Metal particles deposited on thin oxide films have been shown to be suitable model systems for studying structure-reactivity relationships of metal catalysts. A detailed understanding of the surface structure of the oxide films is a crucial prerequisite. It has been previously shown that well-ordered FeO(111), Fe3O4(111) and alpha-Fe2O3(0001) films can be prepared on a Pt(111) substrate in a controllable manner. In this presentation, we report on the determination of the surface structure of these iron oxide films using scanning tunneling microscopy, temperature programmed desorption and vibrational spectroscopy of CO as a probe molecule. In particular, we have found that the Fe3O4(111) surface is terminated by 1/2 monolayer (ML) of iron, with an outermost 1/4 ML consisting of octahedral Fe2+ cations situated above a 1/4 ML of tetrahedral Fe3+ ions. The most strongly bound CO, which desorbs at 230 K, is assigned to adsorption to Fe3+ cations present at the step edges, whose geometry is predicted on the basis of coordinative unsaturation and excess surface charge concepts. For the alpha-Fe2O3(0001) surface, experimental and theoretical evidence is presented which shows that the hematite may be terminated with ferryl (Fe=O) groups, which has never been considered for iron oxide surfaces. In addition, the structure and adsorption properties of metals (Pd, Au) deposited on these films are studied. For example, CO is found to react with lattice oxygen of Fe3O4 at the Pd/oxide periphery. Oxygen adsorption at elevated temperatures resulted in structural changes of the system. The results for the model catalytic systems supported on the iron oxides are compared with data previously obtained for other (non-reducible) oxide films.

3:40pm **SS2-MoA6 Role of Dichlorocarbene in the Surface Chemsitry of Halomethanes on Fe@sub 3@O@sub 4@(111)-(2X2) ; a Comparative Thermal Desorption Study***,* ***Y. Le,*** *G.G. Totir, G.W. Flynn, R.M. Osgood,* Columbia University

Iron-oxide surface chemistry plays an important role in understanding chemical routes for the environmental degradation of chlorinated halocarbons. An earlier study had shown the importance of dichlorocarbene in controlling the thermal reaction products for CCl@sub 4@ chemisorbed on magnetite-terminated hematite surfaces. In this talk, we report on an investigation of the surface chemistry of CCl@sub 4@, CBr@sub 2@Cl@sub 2@, and CH@sub 2@Cl@sub 2@ on a UHV-prepared Fe@sub 3@O@sub 4@(111)-(2X2) selvedge of single-crystal @alpha@-Fe@sub 2@O@sub 3@ (0001). Our experiments use UHV, temperature programmed reaction and desorption (TPR/D) measurements of dosed surfaces, along with LEED and Auger probes. The TPR/D spectra show that dissociative formation of dichlorocarbene, followed by its reaction with lattice oxygen and other adsorbed surface species, is central to the surface chemistry of halocarbons in general, and of halomethanes in particular on the (2X2) reconstructed surface of hematite. The specific branching ratios of the various desorbed products including metal-halides are compared for adsorbed CCl@sub 4@, CBr@sub 2@Cl@sub 2@, and CH@sub 2@Cl@sub 2@ on the (2X2) surface. Our experiments show clearly the importance of CCl@sub 2@ intermediates in these surface reactions.

4:00pm **SS2-MoA7 Methyl Radical Chemistry on Clean and UO@sub3@-Covered Single Crystal Hematite Surfaces***, L. Liu,* Columbia University*; P.C. Stair,* Northwestern University

The partial oxidation of methane over oxide catalysts is controlled by the surface reaction of methyl radicals. Methyl radical chemistry was studied on two model surfaces in UHV: Clean, (0001) orientation single crystal hematite and UO@sub 3@ supported on a crystalline hematite thin film. Temperature Programmed Desorption (TPD) showed that methyl radicals adsorb on the Fe@sub 3@O@sub 4@ (111)-terminated hematite (0001) surface at 300 K and desorb intact at higher temperatures. At saturation coverage, the XPS C(1s) line position is consistent with methoxide ions on the surface, and the carbon-surface bond energy determined by threshold TPD analysis is similar to the C-O bond energy of surface methoxide ions. In contrast, methyl radicals produce only very small desorption features on the biphase-terminated hematite (0001) surface. The coverage of adsorbed methyl was obtained by quantification of the TPD data. Saturation coverage was 1x10@super 14@/cm@super 2@ on the Fe@sub 3@O@sub 4@ (111)-terminated surface but only 3.7x10@super 12@/cm@super 2@ on the biphase-terminated surface, consistent with adsorption on regular surface sites and defect sites, respectively. Since the two surfaces both contain Fe@super 2+@, Fe@super 3+@, and O the differences in methyl radical adsorption must be due to differences in surface structure. Based on an analysis of the structures reported in the literature it is proposed that methyl radicals adsorb on surface oxygen atoms with a dangling bond perpendicular to the surface plane on the Fe@sub 3@O@sub 4@ (111)-terminated surface. On the hematite-supported UO@sub 3@ surface, partial oxidation products, such as methanol, formaldehyde, and CO were identified by TPD. XPS quantification indicates that UO@sub 3@ forms a monolayer structure on the hematite support. The increased reducibility of UO@sub 3@ compared to hematite is responsible for the change in surface chemistry. A surface methoxide ion is the proposed reaction intermediate.

4:20pm **SS2-MoA8 Characterization of the Co@sub 3@O@sub 4@(111) Single Crystal Surface***, **E.M. Marsh**, M.A. Langell,* University of Nebraska-Lincoln

The (111) face of the Co@sub 3@O@sub 4@ single crystal has been characterized using Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and low-energy electron diffraction (LEED) to establish the cleanliness, composition, and order of the (111) surface. The vibrational modes of the Co@sub 3@O@sub 4@(111) face were then investigated by high-resolution electron energy loss spectroscopy (HREELS) and the Fuchs-Kliewer phonon spectrum was obtained with an incident electron energy of 3.77 eV. Data taken on the (111) surface has been compared to previously reported values taken from the (110) surface of the Co@sub 3@O@sub 4@ single crystal. HREELS was also used to study the vibrational modes of H@sub 2@O as an adsorbate on the surface to test the accuracy of the log-deconvolution algorithm in removing the multiple scattering modes of the phonon spectrum.

4:40pm **SS2-MoA9 The Interaction of Carbonyls with Oxide Surfaces: The Adsorption of Formaldehyde on CeO@sub X@(111)***, J. Zhou, **D.R. Mullins**,* Oak Ridge National Laboratory

Formaldehyde, CH@sub 2@O, chemisorbs on both oxidized and reduced cerium oxide surfaces. Near-edge X-ray Absorption Fine Structure (NEXAFS) and synchrotron-excited Soft X-ray Photoelectron Spectroscopy (SXPS) indicate that chemisorption occurs through the formation of a dioxymethylene, CH@sub 2@O@sub 2@, intermediate. On the fully oxidized surface this intermediate is weakly bound and results in molecular formaldehyde desorption between 200 K and 300 K. On a reduced cerium oxide surface the intermediate is more strongly adsorbed and desorbs as formaldehyde near 460 K. Some of the dioxymethylene disproportionates producing formate and methoxy intermediates above 450 K. These intermediates dissociate to form H@sub 2@ and CO products above 550 K. At large formaldehyde exposures polymerization occurs on both the oxidized and reduced ceria surfaces. The polymer decomposes to produce formaldehyde between 300 K and 400 K. The adsorption of formaldehyde, which occurs through the conversion of the carbonyl to carbondioxy on the oxide surface, is contrasted with the adsorption of methanol in which the hydroxyl bond is broken and methoxy is formed on the ceria. The methoxy group is more stable than dioxymethylene on the ceria surface and leads to decomposition products above 560 K rather than the recombinative desorption of methanol. 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.

5:00pm **SS2-MoA10 Structure and Reactivity of the Positively and Negatively Poled Surfaces of LiNbO@sub 3@(0001)***, **M. Li**, D. Liao, E.I. Altman,* Yale University

The effect of ferroelectric poling direction on the structure and reactivity of the LiNbO@sub 3@(0001) surface was studied using reflection high energy and low energy electron diffraction, x-ray and ultraviolet photoelectron spectroscopy (XPS and UPS), ion scattering spectroscopy, and temperature programmed desorption (TPD). The surfaces were prepared by annealing at 1175 K in air at atmospheric pressure and then cleaned by exposure to oxygen plasmas in UHV. Following this procedure, both the positive and negative surfaces gave (1x1) diffraction patterns. No evidence of reconstructions was observed suggesting that both surfaces are bulk terminated with the negatively poled surface exposing Li ions and the positive surface Nb ions, in contrast to prior work that suggested an oxygen termination for both surfaces that would require a reconstruction to maintain the proper stoichiometry. Photoelectron spectra also showed little difference between the positive and negative surfaces with both showing Nb only in the 5+ oxidation state, and valence level spectra with nearly identical emission due to O 2p derived states and no emission in the bandgap due to reduction. These results are also in contrast to a prior study that suggested reduction of the Nb ions near the negatively poled surface. Differences in reactivity of the two surfaces towards CO@sub 2@, water, and 2-propanol is being characterized using TPD along with XPS and UPS.

Thin Films
Room 306 - Session TF+NS-MoA
Focused Beam Processing & Fabrication

Moderator: J.D. Fowlkes, University of Tennessee

2:00pm **TF+NS-MoA1 Beam-Induced Nano-Structuring for Advanced Mask Repair***, **T. Liang**,* Intel Corporation **INVITED**

Photomask repair is a process of editing local pattern structures by adding or removing materials in order to restore a defective mask to good lithographic condition and, in many instances, it is an enabling step for yielding a defect-free mask. Beam-induced nano-structuring has been developed for such process with the use of photons, ions and electrons. However, it has become ever more challenging to repair advanced photomasks because of the limited extendability of these technologies to meet the critical defect specifications and tight edge placement. Specifically, the use of aggressive optical proximity correction structures, resolution enhancement techniques, such as phase-shifting, and entirely new types such as EUV reflective masks has placed a great need for stringent lateral and vertical dimensional control. A capable repair process removes the defect with sufficient placement precision while at the same time preserves the optical integrity of the repaired site. This essentially requires also a damage-free process. Mask shops have put ever increasing emphasis and effort in mask repair at the back end of the production line to fix every defect possible in order to restore an otherwise defective mask. This invited talk will present an overview of advanced mask repair and the lithographic requirements, followed by an assessment of four repair technologies by comparing their respective uniqueness and limitations. The discussion of underlying mechanisms for different repair processes will provide an insight to the fundamental capabilities and ways for further improvements. Detailed descriptions will be given for examples representing binary Cr-on-glass, phase-shifting and EUV masks including repair qualification. I will present our recent progress in electron beam mask repair development and discuss future directions in mask repair using nano-structuring technologies to support the aggressive lithography roadmap

2:40pm **TF+NS-MoA3 Electron Beam Induced Processing Techniques for Advanced Lithography Mask Repair***, **D.A. Smith**,* University of Tennessee, Knoxville*; J.D. Fowlkes,* University of Tennessee, Knoxville, US*; T. Liang,* Intel Corporation*; P.D. Rack,* University of Tennessee, Knoxville

Producing defect-free photomasks for semiconductor applications is a critical and challenging operation. Enabling nano-processes are being developed for mask repair to meet the defect requirements for advanced 193nm and EUV lithography. To this end, we are investigating electron beam induced deposition (EBID) and etching (EBIE) techniques for mask repair involving material deposition and removal, respectively. The EUV masks are typically composed of multi-layer Mo-Si on a quartz-like substrate, capped with a Ru etch stop layer with an overlaying TaBN absorber layer. For material removal, an etchant vapor such as XeF2 or NF3 is flowed over the mask surface in an SEM in the presence of an electron beam. The electron beam interacts with the etchant gas to produce an electron induced etch effect, allowing material removal at a controlled rate with nano-scale precision. Repair operations involving deposition are typically carried out with a precursor gas such as cyclopentadienylplatinum (IV)-trimethyl (CpPtMe3) which dissociates under an electron beam and adsorbs to the substrate. This presentation will demonstrate the results of a study involving the optimal operating conditions for controlled etching and deposition, including an analysis of the sidewalls, roughness, and spontaneous etching. Monte-Carlo based computer simulations of the material deposition will also be employed to describe the effects of varying system parameters such as operating voltage, gas pressure, current and time.

3:00pm **TF+NS-MoA4 Reduction of Laser-Induced Roughness in a-Si:H Surfaces for Vacuum Compatible Lithography***, **R.N. Jacobs**,* US Army RDECOM CERDEC Night Vision and Electronic Sensors Directorate, 22060*; E.W. Robinson, A.J. Stoltz, J.H. Dinan,* US Army RDECOM CERDEC Night Vision and Electronic Sensors Directorate*; L.G. Salamanca-Riba,* University of Maryland, College Park

A vacuum compatible lithography technique has recently been demonstrated, whereby amorphous hydrogenated silicon (a-Si:H) films are used as a resist. Following plasma deposition of the a-Si:H film, poly-Si patterns are generated on the surface by excimer laser exposure through a projection mask. Development is then carried out by hydrogen plasma etching for which etch selectivities of over 1000:1 have been achieved for a-Si:H and poly-Si regions.@footnote 1@ However the rms roughness induced by excimer laser irradiation can be well over 10 times that of the as-deposited a-Si:H surface. This is problematic because the roughness may be transferred to underlying device layers during subsequent pattern transfer plasma etching. We have developed a step-wise laser irradiation procedure that results in a reduction of surface roughness by an order of magnitude to a level of ~1 nm (rms). This value is approximately equal to the surface roughness in the as-deposited a-Si:H film. The irradiation procedure uses multiple pulses with progressive increases in the energy density, in contrast to single high energy density pulses used previously. Transmission electron microscopy and Fourier transform infrared spectroscopy are used to understand and confirm the mechanism behind this process. Our data suggests that the observed reduction in roughness is due both to smaller grain sizes and to a slow rate of H removal from the film surface. While useful for a-Si:H vacuum-lithography processing, our results also hold significance for other applications of laser processed a-Si:H, even where different film properties may be desired. @FootnoteText@ @footnote 1@R.N. Jacobs, A.J. Stoltz, J.H. Dinan, and L. Salamanca-Riba, J. Vac. Sci. Technol. B, 22 1071 (2004).

3:20pm **TF+NS-MoA5 Maskless, Direct-Write Nanolithography using Electron Beam-Induced Deposition***, **S.J. Randolph**,* University of Tennessee, Knoxville*; J.D. Fowlkes,* University of Tennessee, Knoxville, US*; P.D. Rack,* University of Tennessee, Knoxville

Several groups have investigated electron beam-induced deposition (EBID) as a nanoscale direct-write fabrication technique. The EBID process is similar to focused ion beam processing; however deleterious damage associated with ion implantation is mitigated when using an electron beam. Our group has been investigating this technique as a tool for rapid nanoscale device prototyping as well as for device and lithography mask repair. More recently, we have investigated EBID as a technique to be coupled with a massively parallel electron beam lithography concept-the so-called Digital Electrostatic E-beam Array Lithography (DEAL) system. The goal is to develop an alternative ultra-thin resist scheme for the DEAL low energy electron beam lithography system. We have developed a single layer and bilayer resist scheme using a tetraethylorthosilicate (TEOS) and tungsten hexafluoride precursors to deposit SiO@sub x@ and tungsten resist layers. In this presentation our experimental procedure and EBID system will described and the DEAL lithography concept briefly reviewed. The fundamental EBID process will be explained, and we will describe the relevant EBID parameters that affect the single and bilayer EBID resist schemes. The effects of secondary, backscattered, and forward scattered electrons on the resolution and exposure requirements will also be explained, and dose requirements for optimum exposure as a function of beam energy will be illustrated. Pattern transfer of sub-100 nm features requires excellent control of etch selectivity and profile control. The effects of RIE parameters such as pressure, power, and chemistry as they are related to etch selectivity and profile will also be presented.

3:40pm **TF+NS-MoA6 Focused Ion Beam Sculpting of Curved Shapes in Metals and Amorphizable Solids***, **D.P. Adams**, M.J. Vasile,* Sandia National Laboratories

We describe how focused ion beams can be used to sculpt predetermined micron-scale, curved shapes in a variety of initially planar solids. Using a vector-scanned focused Ga ion beam system, we sputter different shapes including hemispheres, paraboloids and sine waves having dimensions from 1-50 microns. Ion sculpting is accomplished by varying pixel dwell time (i.e., dose) within individual boustrophedonic scans. The pixel dwell times determined for a given shape account for the material-specific, angle-dependent sputter yield, Y(theta), the beam current and the ion beam spatial distribution. We highlight new results that show how this sculpting technique can be applied to a large set of materials. Using appropriate sets of dwell times, we sculpt semiconductors (Si, C) amorphized by the high-energy beam, and single crystal metals (Au, W) that remain crystalline with ion exposure. The ion-milled features, in most cases, match the intended shape with milled feature depths repeatedly within 5% of intended values. Finally, we describe techniques that minimize the deleterious effects of redeposition. This includes a method that determines the optimal range of pixel dwell times and research of gas-assisted FIB sculpting techniques.

4:00pm **TF+NS-MoA7 Focused Electron and Ion Beam Processing and Fabrication***, **J. Melngailis**,* University of Maryland*; I. Utke,* EMPA, Thun, Switzerland*; P. Hoffmann,* EPFL, Lausanne, Switzerland **INVITED**

Beams of electrons and ions are now fairly routinely focused to dimensions in the nanometer range. Since the beams can be used to directly alter material, they represent direct nanofabrication tools. We will focus here on direct fabrication rather than lithography which is indirect in that it uses the intermediary of resist. In the case of both ions and electrons material addition or removal can be achieved using precursor gases. In addition ions can also alter material by sputtering (milling), by damage, or by implantation. Many material removal and deposition processes employing precursor gases have been developed for numerous practical applications, such as mask repair, circuit restructuring and repair, and sample sectioning. In many cases the minimum dimensions at which these processes can be realized are considerably larger than the beam diameters. The detailed atomic level mechanisms responsible for the precursor gas activation have not been studied in detail in most cases. We will review the state of the art and level of understanding of direct ion and electron beam fabrication and point out some of the unsolved problems. We will present recent results on beam deposited contacts to carbon nanotubes, nanowires and nanofibers.

4:40pm **TF+NS-MoA9 Sub-Micron Features Using a Focused Ion Beam and Novel Resist Structures***, **M.H. Ervin**,* U.S. Army Research Laboratory

Typically, sub-micron features are written with an e-beam lithography tool. However, e-beam tools are very expensive and availability is an issue. A method for writing sub-micron features (e.g. short gate-length contacts) using a focused ion beam (FIB) is described. It is not just a matter of milling a pattern into any resist. To avoid sputtering the substrate, the mill has to be incomplete, and the partially milled resist may be cross-linked due to the ion irradiation damage. The cross-linked resist is then resistant to solvent development or plasma ashing. This might make it useful as a negative resist, but for positive resist applications write times would be problematic. Instead, two metal films are deposited on top of the resist. The top layer (e.g. Au) is cut through by the FIB to form the pattern, and the underlying layer (e.g. Ti) is the backstop layer which prevents the FIB Ga ions from penetrating through to the resist. The backstop layer is then selectively wet etched. The etch is allowed to produce an undercutting of the pattern layer features for good lift-off. Similarly, the underlying resist can be plasma ashed to expose the substrate. One has to be careful with the ashing temperature to prevent blistering of the resist/metal layers. Subsequent metallization and lift-off can produce features below a quarter micron. Of course, if the substrate is vulnerable to resist solvents, one could omit the resist entirely if the backstop layer can be used to provide lift-off at the end. Another potential advantage for sensitive substrate materials, is that the substrate is never irradiated with ions or electrons as is the case in e-beam lithography.

Science of Semiconductor White Light Topical Conference Room 310 - Session WL-MoA

Science of Semiconductor White Lighting

Moderator: K.H.A. Bogart, Sandia National Laboratories

2:00pm **WL-MoA1 Improving the Brightness of GaN-based Light Emitting Diodes in the Green**, ***C. Wetzel***, *T. Detchprohm,* Rensselaer Polytechnic Institute **INVITED**

Technological innovations to address impeding energy cost raises are of high priority for global economics. Generating white light without the heating losses of light bulbs by means of semiconductor light emitting devices is a prime opportunity to reduce the energy consumption for lighting -- about 20% of the total energy consumption in the US -- by an estimated 28%. Alloys of GaInN offer the prospect for high power light emitters across the entire visible spectrum. While high performance red LEDs have been developed in AlGaInP materials, blue GaInN LEDs have shown major progress in recent years. The immediate challenge is to increase performance throughout the green from 520 nm to 550 nm. Based on detailed spectroscopic bandstructure characterization of GaInN/GaN alloys and quantum wells we have identified materials and device design parameters for high power LED dies emitting in this range. We developed a production scale epitaxial growth process by metal organic vapor phase epitaxy for 525 nm dominant wavelength at typical 1.7 mW at 20 mA in (350 µm)@super 2@ dies. In a (400 µm)@super 2@ design we reach values of 2.5 mW in unencapsulated die. This corresponds to 5.0 mW upon proper encapsulation and 6 to 8 mW for flip-chip processed devices. We provide an analysis of the performance limitations imparting further development towards higher power and higher efficiency devices. Despite respectable performance there is ample of headroom for improvement in the internal light generation efficiency which furthermore can be enhanced by improvements to the light extraction. We present our approach within the framework of significant future energy savings by solid state white light generation.

2:40pm **WL-MoA3 Indium Incorporation Studies for Blue and Green Emitting Multi-Quantum Wells and Light Emitting Diodes**, ***D.D. Koleske***, *S.R. Lee, A.J. Fischer, M.H. Crawford, M.E. Coltrin, M.J. Russell, K.C. Cross,* Sandia National Laboratories

While the promise for tuning the bandgap from 0.7 to 6.2 eV in the group III nitride materials system exists, achieving wavelengths greater than 530 nm is difficult due to several factors. These factors include the disparate growth conditions that must be used for In incorporation, especially temperature, and the lattice mismatch between GaN and InGaN alloys, which may induce compositional instability and decrease structural ordering. The issue of In incorporation becomes particularly important for improving light emission for green LEDs, where the internal quantum efficiency is significantly less than for blue LEDs. Currently, we are investigating the growth of InGaN multi-quantum wells (MQWs) with the aim of understanding how the growth conditions influence In incorporation. The MQW structure is analyzed using x-ray diffraction and dynamical diffraction theory is used to determine the In content and quantum well thickness. Photoluminescence and fabrication of simple LEDs were used to characterize the photo- and electro-luminescence properties of the films. We explored two different growth regimes for improving In incorporation into the QWs. The first growth regime involved growing the MQWs with very high growth rates to capture and bury the In before it desorbs. In this fast growth regime, we were able to incorporate up to 18 % In into the MQWs at 770 °C, leading to 470 nm LED emission. A subsequent reduction of the growth temperature to 725 °C produced green LEDs emitting at 510 nm. The second growth regime involves slower growth rates and lower growth temperatures which allows for increased In residence time on the surface, potentially leading to higher In content in the MQWs. Advantages and disadvantages of both growth regimes will be discussed with a focus on identifying the growth regime that enables the highest luminescence efficiency in green MQWs and LEDs

3:00pm **WL-MoA4 Temperature Measurement and Control during Group-III Nitride MOCVD**, ***J.R. Creighton***, *D.D. Koleske, C.C. Mitchell, M.J. Russell,* Sandia National Laboratories

Accurate temperature measurement during group-III nitride MOCVD is difficult due to the broad spectral transparency of the substrates and epitaxial layers. In fact, there is no readily available method that measures the true surface temperature during deposition on sapphire substrates. We have developed a pyrometer in our single-wafer research reactor that operates near the high-temperature bandgap of GaN, thus solving the transparency problem once a ~1 micron thick GaN epilayer has been established. The system collects radiation in the near-UV (380-415 nm) and has an effective detection wavelength of ~405 nm. Near 1000°C, the RMS temperature noise of the system is <0.1°C, and at 800°C the RMS temperature noise is <0.5°C. By simultaneously measuring the reflectance, we can also correct for emissivity changes when films of differing optical properties (e.g. AlGaN) are deposited on the GaN template. By employing the virtual interface method, the reflectance measurement can also be used to monitor growth rates and compute optical properties of the thin films. We have recently modified the pyrometer hardware and software to enable measurements in one of our commercial Veeco D-125 multiwafer MOCVD systems. A method of synchronizing and indexing the detection system with the wafer platen was developed so signals only from the desired wafer(s) could be measured, while rejecting thermal emission signals from the platen. The Veeco D-125 also has more limited optical access, in comparison to our research reactor, so the front end collection optics required a redesign and optimization. Despite the losses in optical throughput and duty cycle, we are able to maintain good performance from 750-1100°C. (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 **WL-MoA5 Color Conversion in Light Emitting Devices using Nonradiative Energy Transfer**, ***M. Achermann***, *M.A. Petruska, S. Kos, D.L. Smith,* Los Alamos National Laboratory; *D.D. Koleske,* Sandia National Laboratories; *V.I. Klimov,* Los Alamos National Laboratory **INVITED**

Using modern colloidal chemistry, semiconductor nanocrystals (NCs) can be fabricated with nearly atomic precision in a wide range of sizes and shapes. NCs exhibit high photoluminescence (PL) quantum yields and narrow size-controlled emission lines, and they can easily be manipulated into various two-dimensional (2D) and 3D assemblies. All of these properties make NCs attractive building blocks for applications in various optical technologies including light-emitting devices. One problem associated with realizing NC-based light emitters is that the electrical injection of carriers into NCs is complicated by the presence of the insulating passivation layer. All previous attempts to electrically contact NCs have utilized hybrid inorganic/organic composites comprising conducting polymers. However, the performance of these devices is severely limited by low carrier mobilities in both NC and polymer components and poor polymer stability with respect to photooxidation. Here, we present an alternative, "noncontact" approach to injecting carriers into NCs via nonradiative energy transfer (ET) from a proximal epitaxial quantum well (QW). Monitoring time and spectrally resolved PL dynamics, we observe an efficient energy outflow from the QW, which is accompanied by a complimentary energy inflow into a dense monolayer of NCs assembled on the top of the QW. The measured ET rates are very fast and should allow for the efficient pumping of NCs not only in the spontaneous but also in the stimulated emission regime.

4:00pm **WL-MoA7 Photonic Crystals for Enhanced Light Extraction in InGaN LEDs**, ***A.J. Fischer***, *D.D. Koleske, G.R. Hadley, J.R. Wendt, R.J. Shul,* Sandia National Laboratories; *J.J. Wierer, M.R. Krames,* Lumileds Lighting **INVITED**

In order to realize semiconductor-based white lighting with efficacies of 200 lm/Watt, InGaN light emitting diodes (LEDs) must have wall plug efficiencies on the order of 50% or better. Even when internal quantum efficiencies approach 100%, most LEDs suffer from poor light extraction efficiency. The majority of photons generated inside of a high index semiconductor bounce around due to total internal reflection where they have a high probability of being reabsorbed. Many methods have been used to improve the extraction efficiency of LEDs including chip shaping, surface texturing, and resonant cavity LEDs. Photonic crystals can also be used to enhance extraction efficiency by either suppressing emission of light into waveguiding modes or by extracting waveguiding modes via Bragg scattering. We have fabricated InGaN LEDs with an incorporated photonic lattice by etching holes into the GaN surface. E-beam lithography was used for submicron pattern transfer and Cl-based inductively-coupled plasma reactive ion etching was used to etch holes in GaN. For these LED structures, the photonic lattice improves light extraction by extracting light emitted into waveguiding modes. An overview of light extraction from InGaN LEDs will be given as well as recent device results from InGaN photonic crystal LEDs. Sandia National Labs is a multi program laboratory operated by Sandia Corporation, a Lockheed Martin Company for the United States Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000.

4:40pm **WL-MoA9 CdSe Nanocrystal Light Emitting Diodes: Toward Full Spectrum White Light Generation***, **A.H. Mueller**, E.A. Akhadov, M.A. Petruska, M. Achermann, V.I. Klimov, M.A. Hoffbauer,* Los Alamos National Laboratory

Semiconductor nanocrystals (NCs) of CdSe exhibit light emission across the visible light spectrum with optical excitation quantum efficiencies (QE) exceeding 80%. With the emission wavelength determined by the NC size, blends of different size NCs as chromophores can be used to generate a broadband white light spectrum. The ultimate efficiency of such a source will be determined not by the NC's QE, but by the efficiency of the excitation source. Alternatively, direct electrical excitation of NCs can eliminate inefficiencies in photon absorption and re-emission by the chromophore. Previous electrically pumped NC-LEDs used hybrid polymer/NC architectures to achieve direct injection of carriers into the active layer. Efficiency in these devices is limited by the poor carrier mobilities in the organic components, and they exhibit short operative lifetimes due to photooxidation of the injection layers. These barriers to high efficiencies can be removed by combining inorganic, semiconducting injection layers of GaN with NCs, but this combination is difficult to achieve due to the harsh conditions typically needed for GaN film growth. We have succeeded in fabricating NC LEDs by encapsulating single- and multilayers of CdSe/ZnS core/shell NCs in semiconducting GaN thin films. The GaN films are grown using Energetic Neutral Atom Beam Lithography/Epitaxy (ENABLE), a unique thin film growth technique developed at LANL for growing semiconducting nitride films at low temperatures. Layers of NCs were assembled on a p-GaN substrate using Langmuir-Blodgett (LB) techniques and encapsulated with ENABLE grown n-GaN. This structure allows direct injection of carriers into the NCs, resulting in light emission at a wavelength determined by the NC's size. Prototype devices have shown emission from single and multicolor NC layers. Ultimately, assemblies of different size NCs as active regions in these LEDs will permit tailoring their output for generating full spectrum white light

5:00pm **WL-MoA10 Trapped Whispering-Gallery Optical Modes in White Light-Emitting Diode Lamps with Remote Phosphor***, **H. Luo**, J.K. Kim, Y.A. Xi, E.F. Schubert,* Rensselaer Polytechnic Institute*; J. Cho, C. Sone, Y. Park,* Samsung Advanced Institute of Technology, South Korea

Phosphorescence efficiency in high-power white light-emitting diode (LED) lamps is investigated by three-dimensional ray tracing. It is shown that the absorption of the phosphorescence by the LED chip is greatly reduced by employing a remote phosphor, resulting in the improvement of lamp efficiency. However, for lamps with remote phosphor, a significant fraction of the phosphorescence is found to be trapped as whispering-gallery modes propagating along the circumference of the encapsulant, which causes significant optical loss. The whispering-gallery modes, which occur irrespective of the shape of the encapsulation dome, are shown to be sensitively dependent on the diffusivity of the reflector cup employed in the lamp. Dichromatic LED lamps with remote phosphor were fabricated for reflector cups with different diffusivity. The phosphorescence efficiency is found to be improved by up to 27% for a remote phosphor configuration and a diffuse reflector cup. The experimental results are consistent with theoretical ray tracing simulations.

Applied Surface Science
Room Exhibit Hall C&D - Session AS-MoP
Aspects of Applied Surface Science Poster Session

AS-MoP2 Unusual Interdiffusion Reactions in Multilayer ZrO@sub 2@CaO/Fe/Si Thin Films*, H. Piao, L. Le Tarte, L. Denault, J.R. Cournoyer, K. Dovidenko, M. Larsen, J. Osaheni,* General Electric Co., Global Research Center

Interdiffusion reactions in multilayer ZrO@sub 2@CaO/Fe/Si thin film (2mm diameter dot) have been studied using X-ray Photoelectron Spectroscopy (XPS) in combination with Scanning Auger Microscopy (SAM), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The 2mm diameter thin film dots were prepared through a shadow mask by depositing Fe and ZrO@sub 2@CaO sequentially on silicon substrates, followed by thermal treatments. It was found that heating at elevated temperatures resulted in the segregation of the islands on the substrate with the accompanying formation of irregular shaped pits in the film. The diameters of the islands are typically in the range from 100 to 250nm. XPS and SAM results on these islands indicated that the islands are mainly iron silicide coated with Fe, Zr-Ca and Si oxide towards to the surface. The formation of the interfacial iron silicide (FeSi@sub 2@) arising from the bulk interdiffusion of Fe and Si were confirmed by XPS, TEM, and SAD (selected area diffraction) studies. Much more surprising is the surface enrichment of silicon oxide on the whole dot surface. The fast segregation of silicon from the substrate to the surface does not appear to be via bulk interdiffusion. The implications of these findings to the diffusion properties of the thin film will be discussed.

AS-MoP3 Synthesis and Characterization of Spectroscopic Tags Based Surface-Enhanced Raman Spectroscopy (SERS) of BPE Adsorbed on Gold Nanoparticles*, **M.C. Burrell**,* GE Global Research Center

Nanoparticle tags detectable by Raman spectroscopy, due to the surface-enhanced Raman effect (SERS) of adsorbed reporter molecules, have potential applications ranging from biological assays to cellular imaging. This paper describes the surface chemistry considerations, and characterization methods employed, in producing gold nanoparticles with an adsorbed bis(4-pyridyl) ethylene [BPE] reporter molecule. The SERS response of the tags is affected by the size of the gold nanoparticles, the adsorption conditions of the BPE, and co-adsorption of precursors for growth of protective shells. A primary consideration in producing tags is preventing aggregation of the particles, even though the SERS enhancement of individual particles is lower than aggregates. We will present data from Raman spectroscopy, UV-visible absorbance, light scattering, and TEM to used to characterize the tags during the synthesis process.

AS-MoP4 Dimensional Effects of Metal Nanoparticles on Their Characterization by X-ray Photoelectron Spectroscopy*, **D.-Q. Yang**, E. Sacher,* Ecole Polytechnique of Montreal, Canada

X-ray photoelectron spectroscopy (XPS) has been found very useful in the understanding of the electronic states of supported metal catalyst nanoparticles. We give a short review on the photoelectron emission behaviour of nanoparticles deposited on several relatively unreactive substrate surfaces, including highly oriented pyrolytic graphite (HOPG) with varying surface defects densities, and low permittivity polymers. We fix our attention on the (1) photoelectron emission yield enhancement induced by the nanoparticles, (2) photoelectron emission from the shell and the core of the nanoparticles, (3) size-dependent binding energy shifts, (3) Auger parameters, (4) Wagner plots and (5) initial-state and final-state effects on the nanoparticle dimensions and their substrate surface interactions. Intensity ratios, from a given nanoparticle at two different kinetic energies, as well as from nanoparticle and substrate, and their dependences on nanoparticle dimensions, are also explored.

AS-MoP5 Thickness Measurement Of Diamond-Like Carbon (DLC) By Auger Electron Spectroscopy (AES)*, Y. Zheng, **B. Lu**,* Seagate Technology (RMO) Ltd*; G. Selvaduray,* San Jose State University

Abstract-To increase the density of magnetic recoding disks and to protect the magnetic layers from sliding contact and corrosion, it is important to be able to accurately measure the thickness of DLC films. The ability to use AES to measure the DLC thickness on magnetic recording disks was studied. The principle of DLC thickness measurement was based on Beer-Lambert's law. The approach was to construct a working curve by using the thickness of DLC measured by ESCA and the intensities of the carbon and cobalt signals detected by AES to generate the calibration parameter " ". This study demonstrated that the DLC thickness could be measured by AES, employing the intensities of the cobalt signal present in the magnetic layer. Statistical analyses verified that there were no significant differences between the DLC thickness measured by ESCA and those measured by AES.

AS-MoP6 Structural Analysis of a DTHXBQ/Pt(dmg)@sub 2@ on KBr Plate used by TRXPS*, T. Tazawa, **Y. Iijima**,* JEOL Ltd., Japan*; S. Isoda,* Kyoto University, Japan

Recently, with development of thin film technique, analysis of the molecular film which did lamination in a structural analysis of monomolecular film and thickness of several nm has been demanded from X-ray photoelectron spectrometer (XPS). Because this material is formed on flat plate, such as silicon wafer, it is possible to measure with total reflection x-ray photoelectron spectrometer (TRXPS). A location of standing wave changes when it changes in X-ray incidence angle in TRXPS. This change does intensity change of photoelectron intensity, and it is observed. Variation that is to say occurs in photoelectron intensity by an entity location, a difference of angle in the same functional group. Firstly film formation did Pt(dmg)@sub 2@ in thickness of 15nm on KBr plate by this study, and DTHXBQ film (organic compound) formed on that film, after that we measured this organic compound film used by TRXPS. Measurement changed incidence X-rays from 10° to 0°, and we measured photoelectron intensity-dependence of Pt4f, O1s, C1s and N1s for incidence angle of x-ray. The insturment which we used for measurement is JPS-9200 (JEOL Ltd.). Measurement condition is as follows. Excitation x-ray is AlK@alpha@ monochromatic X-ray, x-ray power in measurement is 300W, and energy resolution is 0.8eV. As a result, we were able to decided a location of Pt in Pt(dmg)2,and a structure of Pt(dmg)@sub 2@ and DTHXBQ films on KBr plate.

AS-MoP7 Investigation of Pharmaceutical Packaging Materials using XPS and TOF-SIMS*, **X. Dong**, R.G. Iacocca, J. Janimak, M.C. Allgeier,* Eli Lilly

The surface composition of packaging materials is of great interest to the pharmaceutical community because of potential interactions between the packaging surface and the drug product. The surface sensitivity of XPS and TOF-SIMS makes these techniques ideally suited to the surface characterization of packaging materials. In this work, XPS was utilized to evaluate surface compositions of three Type I glass vials from different sources. The bulk compositions of three glass vials are similar to each other, and the surface of one glass vial is ammonium sulfate treated. To thoroughly understand the surface composition, survey and high resolution spectra, as well as small spot images, were collected from all three samples. The XPS results revealed marked difference in surface compositions of the three vials. Significantly higher amounts of B and Na were detected on one vial than on the other two, suggesting that this glass had been exposed to excessive heat. Sodium sulfate residues were present on the ammonium sulfate treated vial, suggesting the rinsing process performed by the manufacturer is not thorough enough. In addition to glass vials, plastic liners, another commonly used packaging material for Active Pharmaceutical Ingredient (API) powders, were also examined. API stored in plastic liners under different conditions were investigated, and compared to that stored in glass vials using TOF-SIMS. It is obvious that the additives present on the surface of the plastic liner were transferred to the API during storage. The preliminary results also suggest that the increase of additives on the API is consistent with the decrease in surface area. This work clearly demonstrates that XPS and TOF-SIMS are highly valuable techniques in evaluation of pharmaceutical packaging materials, as well as in the investigation of the interactions between drug products and the packaging.

AS-MoP8 Determination of Equivalent Circuits of Surface Structures for XPS Analysis*, **O. Tasci**, U.K. Demirok, E. Atalar, S. Suzer,* Bilkent University, Turkey

XPS analysis of non-conducting samples is usually hampered due to charging, and a great deal of effort has been devoted to minimize it. However, it is also possible to utilize this charging to extract information related with dielectric properties of various surface structures. Determination of equivalent circuit(s) and testing on real samples emerge as essential parts of this analysis. To this end, we have carried out a number of experiments to determine the charging/discharging behavior of various surface structures consisting of Au, Ag, and Pt (metallic), Titania (semiconductor), and Silica (dielectric) Nanoparticles deposited on SiO@sub 2@/Si substrates by XPS. We have also constructed the corresponding equivalent circuits by using the PSPICE program and correlated the output with the experimental data. Our experimental results and their correlation with the model(s) will be discussed in detail.

AS-MoP9 Scanning Probe Microscopy and X-ray Photoelectron Spectroscopy Investigations of Focused Ion Beam-Irradiated Targets*, **K. Archuleta**,* Sandia National Laboratories*; J.L. Fenton,* University of New Mexico*; M.J. Vasile, S. Campin, D.P. Adams,* Sandia National Laboratories*; J.E. Fulghum,* University of New Mexico

Focused ion beam (FIB) techniques have a wide range of applications, from lithographic mask repair and semiconductor analysis to machining of microtools. As FIB prototyping methods are extended to the nanometer scale, the effects of distributed charge resulting from ion implantation/sputtering, modifications in near-surface chemistry, and evolved surface morphology become more relevant to device fabrication and operation. Toward this end, we investigate the residual electronic and chemical properties of ion-exposed areas. High energy (30 keV) focused ion beams are used to expose 100 Âµm wide features in Si, SiO2 and C substrates. Samples are then removed from the FIB system, and the residual surface potential and spatial distributions of charge are analyzed using ex-situ scanning surface potential microscopy and scanning capacitance microscopy. Changes in residual surface potential are evaluated over a large range of ion dose (~1016 -1018 ions/cm2); this includes conditions that lead to target swelling (low fluence) followed by constant-rate sputter erosion (high dose). The evolving chemistry of the near-surface region is also investigated as a function of ion dose. High spatial resolution, x-ray photoelectron spectroscopy provides insight into the changes of near-surface composition that occur during increased gallium ion exposure.

AS-MoP10 The Efficacy of Organosilane Surface Modifications on Distribution of Polar Inorganic Particles within a Nonpolar Polymer Matrix*, **A.K. Wertsching**, T.L. Trowbridge, P.J. Pinhero,* Idaho National Laboratory

Improving the surface interface of nonpolar and polar materials is critical to creating the desired physical properties of hybrid composites. Modification of inorganic particles with various organosilanes has the effect of creating a nonpolar surface on a polar material, which then can be dispersed into nonpolar media. However, choice of organosilane can have radically different results on the composite. The impact of the organosilane upon these composites are examined using scanning electron microscopy (SEM), atomic force microscopy (AFM), scanning Auger microscopy (SAM), and x-ray photoelectron spectroscopy (XPS).

AS-MoP11 Accurate Force Measurements in the AFM: Improvements in the MEMS Electrical Nanobalance Calibration Device*, **J. Portoles**,* National Physical Laboratory and University of Nottingham, UK*; P.J. Cumpson,* National Physical Laboratory, UK*; S. Allen, S. Tendler, P. Williams,* University of Nottingham, UK

Since its invention in 1986 the AFM technique has been a powerful imaging tool, and increasingly an instrument to measure forces of the order of pN to nN. These measurements are important in biological research in the context of the study of specific interactions that affect stability and biological function of macromolecules. The accuracy of those measurements relies largely on the determination of the AFM-cantilever spring constant. Several calibration methods have been developed based on different approaches ranging from dimensional measurements of cantilevers, or static loading to dynamic measurements and Finite Elements simulations. All these methods suffer from poor precision arising from different sources (limited manufacturing control in thickness and elastic properties, difficulties in dynamic modelling, etc) Here a different approach is tested, which doesn't rely on the study of the cantilever systems. All the difficulties concerning elastic constant calibration are "transferred" to a reference system, the Electrical Nanobalance device.@footnote 1@ This is designed as a MEMS device in order to provide accurate calibration of its spring constant by a combination of interferometrical measurements and electrical excitation in vacuum. Once calibrated the spring constant of cantilevers of different materials and geometries can be determined by comparison with the nanobalance device through a simple force-distance measurement performed in air. In this poster we present tests of Electrical Nanobalance MEMS devices, in particular examining the so-called corner-loading problem. @FootnoteText@ @footnote 1@ P J Cumpson and J Hedley, Nanotechnology 14 (2003) 1279-1288.

AS-MoP12 An Investigation of Photoperturbation Effects on Conductive Atomic Force Microscopy*, **M.-N. Chang**, C.-Y. Chen,* National Nano Device Laboratories, Taiwan

Conductive atomic force microscopy (C-AFM) with a high current sensitivity and a high spatial resolution has attracted much interest in mapping two-dimensional current distribution, investigating the local current-voltage characteristics and examining the breakdown properties of the dielectric layer in electronic devices. With atomic force microscopic setup, C-AFM can synchronously provide the current images and the corresponding topographic images. However, it has been revealed that the stray light of AFM laser beam can induce photoperturbations and hence lead to many difficulties in employing scanning capacitance microscopy to investigate carrier distribution and electrical junctions. In this work, we have qualitatively revealed that the AFM laser beam can significantly perturb the local current-voltage spectra and current distribution profiles taken by C-AFM. Studied samples were n- and p-type silicon covered with a thermally grown ultrathin SiO@sub 2@ film. The wavelength of the AFM laser ranges from 620 nm to 690 nm and the output power is 1.0 mW. The C-AFM measurement was performed in an environment with well-controlled temperature and humidity. For p-type sample, it is clearly observed that the onset voltage decreases with the photoperturbation level. The photovoltaic effect and the additional minority carrier density at the edge of the space-charge region can enhance the electric field across the SiO@sub 2@ film. For n-type sample, photoperturbations can lead to a higher injection barrier height for electrons. Experimental results indicate that the photoperturbations induced by the AFM laser beam not only significantly affects the current image of C-AFM, but also reduces the accuracy of the examination of the current-voltage characteristics, in particular for the ultrathin dielectric film on lower band-gap semiconductors, e.g., Si and Si@sub x@Ge@sub 1-x@.

AS-MoP13 Random Fractal Behavior of InGaAs Quantum Dots Using AFM*, **X. Qian**, S.R. Vangala, C. Santeufemio, W.D. Goodhue,* University of Massachusetts*; Y. Park,* Inje University, South Korea

Autocorrelation, height-height difference correlation, and power spectral density (PSD) analysis techniques have been applied to AFM scans of semiconductor materials for years. Recently Fenner et al@footnote 1@ and Krishnaswami et al@footnote 2@ have developed and applied random fractal analysis techniques to AFM image statistics in order to determine the fractal nature of semiconductor surfaces. Here random fractals are used to investigate InGaAs quantum dots. An uncapped single layer InGaAs dot structure exhibited an autocorrelation Hurst parameter of approximate 0.67 with an autocorrelation length of 90 nm and height-height difference correlation length of 56 nm. An uncapped InGaAs dot structure with two buried InGaAs dot layers exhibited an autocorrelation Hurst parameter of approximate 0.45 with an autocorrelation length of 70 nm and height-height difference correlation length of 47 nm. A 220 nm capped three layers InGaAs dot structure on the other hand exhibited an autocorrelation Hurst parameter of approximate 0.9 with an autocorrelation length of 190 nm and height-height difference correlation length of 130 nm. All samples exhibited height-height difference Hurst parameters and power spectral density Hurst parameters of 1 (indicating Gaussian distributions). All images analyzed were 10x10 µm@super 2@ in size. The analysis indicates that as more dot layers are incorporated in the structure, the fractal nature of the over layer increases. This nature is reversed by a thick capping layer. @FootnoteText@ @footnote 1@ D.B. Fenner, J. Appl. Phys., 95(10),5408-5418 (2004)@footnote 2@ K. Krishnaswami, Mater. Res. Soc. Symp. Proc. Vol.829 (2005).

AS-MoP14 Potential Difference Mapping of Molecules and Particles on Insulating Substrate*, **F. Yamada**, T. Matsumoto, H. Tanaka, T. Kawai,* Osaka University, Japan

A lot of research groups are challenging to fabricate molecular devices by using self-assembly of molecules. For this purpose, the knowledge of local surface potential is essential to understand and control the driving force of the self-assembly. However, it is very difficult to measure the electric properties of nano structures of the molecular devices because such devices are created on an insulating substrate. We report here surface potential measurement of DNA and nanoparticle on an insulating substrate. We used the frequency mode non-contact AFM (FM-ncAFM). NC-AFM is able to measure local electrostatic force with high sensitivity and NC-AFM prevents the charge injection induced by tip-sample contact. The measurement reveals that the potential of DNA is higher than mica and sapphire surface. In this experiment, we demonstrated that the NC-AFM enables us to obtain surface potential images of molecules on insulating substrates. We also measured the d(@DELTA@f)/dV images of DNA and Au nanoparticles on mica. We found that the plots of the d(@DELTA@f)/dV as a function of bias voltage give characteristic slopes indicating the dielectric constants of different absorbates. This result means that this measurement can be used to discriminate surface species on an insulating substrate. To discuss about the contrast mechanism of the surface potential imaging on insulating substrate, this result is beyond the understanding based on

Kelvin force microscopy because the surface potential of insulating substrate is indefinable. Then, we calculate electric filed just below the tip apex using finite element method. The calculation results reveals that the electric field just below the tip apex is enough strong to detect the local charge on surface adsorbate even if the substrate is insulator.

AS-MoP15 Surface Structure of Thermal Neutron Absorbing Ni-Cr-Mo-Gd Alloys, ***P.J. Pinhero***, *T.L. Trowbridge, T.E. Lister, R.E. Mizia,* Idaho National Laboratory

A new thermal-neutron-absorbing Ni-Cr-Mo-Gd alloy was developed at the Idaho National Laboratory (INL). The purpose of this alloy is to potentially absorb neutrons liberated from spent nuclear fuel (SNF) and mitigate any issues related to nuclear criticality. The microstructure of this alloy indicates a two-phase structure consisting of the primary Ni-Cr-Mo austenite matrix phase and secondary Ni@sub 5@Gd phase inclusions arising from the precipitation of the austenite-insoluble Gd. Presently, this alloy is under consideration for use within the U.S. Department of Energy (DOE) standardized SNF waste packages. To support the case for this alloyâ?Ts acceptance and understand its more fundamental surface character, studies were undertaken to examine its structure and composition with respect to its bulk properties, the role of oxidation and resulting passivation on its susceptibility to corrode, and finally how these properties are influenced through boron-doping. This paper focuses on the surface structure and composition of the Ni-Cr-Mo-Gd alloy, and its boron-doped brethren, through the use of electron microscopy, electron spectroscopy, and scanning probe microscopy.

AS-MoP16 Information Needed for Improving Sputter Depth Profiling, ***M.H. Engelhard***, *D.R. Baer, D.J. Gaspar,* Pacific Northwest National Laboratory

In a recent survey of needs for improving surface analysis conducted by ASTM Committee E42 on Surface Analysis, nine of the top twenty-five areas of need involved obtaining depth information. Analysts were interested in reference data, reference materials, and guides or protocols for obtaining useful information. Specific requests related to a data base containing relative sputter rates for compound materials and protocols for obtaining depth information for layered samples. Although not highlighted in the survey, accurate comparison of sputtered depths requires knowledge of the sputter rate reproducibility for a specific system before information about the relative sputter rates for different materials is meaningful. In this presentation we will present data on the reproducibility of sputter rates for our Phi Quantum 2000 and show data we have collected on the measured sputter rates for Fe@sub 2@O@sub 3@ and CeO@sub 2@ relative to SiO@sub 2@. We also note that many modern materials for which thickness information is desired are not simple thin films. We have found that apparent sputter rates for nanoporous silica films can be significantly altered (at least for a short term) by sample processing and cleaning methods.

AS-MoP17 Effect of Nitrogen on the Preparation of High Quality TiO@sub2-X@N@subX@ Thin Films as a Photocatalyst, *K. Prabakar, T. Takahashi,* ***T. Nezuka,*** Toyama University, Japan*; T. Nakashima,* Kashiwa Chuo High School, Japan*; Y. Kubota,* Yokohama City University, Japan*; A. Fujishima,* Kanagawa Academy of Science and Technology, Japan

Titanium dioxide (TiO@sub2@) has been a well-known photocatalytic material for the past few decades, but needs UV light, so the development of a photocatalyst sensitive in visible light irradiation condition is important for indoor use. The main approaches were substitutional doping of nitrogen, since the TiO@sub2-X@N@subX@ films absorbs visible light, we have decided to use the visible light active TiO@sub2-X@N@subX@ film for the development of photocatalysis under controlled deposition parameters. TiO@sub2-X@N@subX@ films were deposited on glass substrates by reactive magnetron sputtering with different Ar+O@sub2@ mixture (7:3, 8:2 and 9:1) as reactive gas at different nitrogen flow ratio. Interestingly, the absorbance spectrum of the TiO@sub2-X@N@subX@ revealed that that the amount of nitrogen doped in the TiO@sub2@ films is not influenced by the nitrogen gas flow ratio but greatly depends on the sputtering pressure and substrate temperature. The properties of the films, including crystallinity, surface morphology and light absorption capability are influenced by the sputtering pressure, substrate temperature and post deposition annealing. The absorption edge shift to the visible light region and the new absorption shoulder at around 430 nm were observed for the films deposited at 0.1 Pa and annealed at 400 ° C and that they were related to the nitrogen doping, since TiO@sub2@ does not absorb such visible light regions. The photocatalytic degradation of organic compounds were analyzed and discussed as a function of deposition parameters such as gas flow ratio, substrate temperature, sputtering pressures and source to target distance. The efficiency of the photocatalytic activity of the TiO@sub2-X@N@subX@ thin films are calculated at different light intensity, solution concentration and the results are discussed.

AS-MoP18 Sputtering Pressure Dependent Photocatalytic Properties of TiO@sub2@ Thin Films, ***T. Takahashi***, *K. Prabakar, T. Nezuka,* Toyama University, Japan*; T. Nakashima,* Kashiwa Chuo High School, Japan*; Y. Kubota,* Yokohama City University, Japan*; A. Fujishima,* Kanagawa Academy of Science and Technology, Japan

Titanium dioxide (TiO@sub2@) has been well-known as a photocatalyst. The objective of this research was to study the photocatalytic degradation of methanol and methylene blue at different light intensity and concentration by the effect of TiO@sub2@ thin film deposition parameters. The TiO@sub2@ films were deposited on glass substrate by direct current reactive magnetron sputtering under various total sputtering gas pressures (P@subS@) of 0.2, 0.5, 0.8 and 5 Pa and at the target to substrate distance (D@subT-S@) of 40 and 70 mm respectively with oxygen argon flow ratio 7:3 and 8:2 to find the optimum conditions to deposit the films with high photocatalytic activities. Structural factors dominating the photocatalytic activities were investigated in detail in relation to the sputter deposition processes. The films deposited at P@subS@ of 0.2 and 0.5 Pa and D@subT-S@ of 40 mm showed polycrystalline anatase structure, but, in the case of D@subT-S@ as 70 mm, only the film deposited at P@subS@ of 0.2 Pa showed the polycrystalline anatase structure. The films deposited at P@subS@ of 0.2 and 0.5 Pa showed decreasing tendency in the optical band gap energy and performed high photocatalytic activities. Such enhancement of the photocatalytic activity was considered to be correlated with the less number of defect level generations caused by the bombardment of the high-energy particles due to the long mean free path. The band gap energy was found to decrease from 3.4 to 3.1 eV for the TiO@sub2@ films deposited at lower P@subS@ as well as the D@subT-S@ was 40 mm, because of the higher crystallinity compared to the films deposited at high pressures and longer D@subT-S@. In addition to this, the films deposited at D@subT-S@ of 70 mm showed the decrease in density consequently increase in the optical band gap energy. The efficiency of the TiO@sub2@ catalysis was studied to evaluate the economic viability of this technique.

AS-MoP20 Development of a Plasma Process for Improving Optical and Biocompatible Properties of Contact Lens, *M. Dhayal, C.H. Kim,* ***C.H. So,*** Dongshin University, South Korea

The use of contact lenses is limited by its optical and biocompatible properties of materials and coatings used in the process. Therefore, a new process has been developed to improve the optical properties of contact lens materials with biocompatibilities. In this work the effect of different SiO2 and TiO2 coatings on polymeric or non polymeric material characterized for optical and biological properties. The TiO2 coatings has advantage in having low reflectance (<0.5 %) and on this coating on soft substrate materials (PMMA) can prevent from hard scratching, effect of temperature variation etc. The particular interest is in quarter wavelength thickness (100 to 200 nm) films of low reflectance for visible light wavelength (400 to 700 nm) having high optical uniformity, temperature stability, resistance to environmental and mechanical degradation. The optical properties of films (such as reflectance, refractive index) has been measured using optical spectrometer, XRD used to characterized the surface structure of films where as XPS used for surface sate analysis. Quality of composition and grain size of micro structure of coatings layer (surface) also examined using SEM, AFM.

AS-MoP21 UHV Studies of Silicon Carbide Gas Sensors with Catalytic Platinum Gates, ***Y.H. Kahng***, *R.G. Tobin,* Tufts University*; R.N. Ghosh,* Michigan State University

We have studied the sensing response and surface chemistry of silicon carbide (SiC)-based gas sensors with catalytic platinum gates, in ultrahigh vacuum. Silicon carbide's large bandgap (2.4 - 3.3 eV), native oxide, and rugged physical properties make it an attractive material for use in extreme environments, including corrosive gases and temperatures up to 1000 K. Possible applications include coal burners and gasification facilities. Catalytic-gate devices based on SiC have shown response to hydrogen and hydrogen-containing gases over a wide concentration range, but details of the transduction mechanism are not fully understood. We report UHV studies of the surface chemistry and sensing behavior of prototype Pt-SiO@sub 2@-SiC sensors, aimed at a detailed understanding of the role of the catalytic gate in abstracting hydrogen from the analyte, providing pathways from the gate surface to the oxide interface, and catalyzing oxidation of hydrogen desorbed from interface sites. Issues investigated include sensor response to varying partial pressures of hydrogen and oxygen and changes in gate properties resulting from gas exposure at elevated temperatures (600 - 800 K). Because sulfur is a contaminant in most fossil fuels and a notorious poison for catalysts, effects of sulfur contamination have also been studied.

AS-MoP22 Electrochemical Spectroscopic Studies of New Materials for PEM Fuel Cells*, **P.C. Wong**, D. Susac, L. Zhu, A. Sode, M. Teo, D. Bizzotto, R. Parsons, K.A.R. Mitchell,* University of British Columbia, Canada*; S.A. Campbell,* Ballard Power Systems, Canada

A new approach for designing potential catalysts for proton exchange membrane (PEM) fuel cells involves characterizing surfaces of thin film materials fabricated as possible cathodes, to avoid the expense and slow oxygen reduction kinetics associated with platinum. This paper will describe studies, especially with X-ray photoelectron spectroscopy (XPS) and scanning Auger microscopy (SAM) of metal chalcogenide surfaces before and after electrochemical activity. Particular examples will be presented for thin films formed by cobalt and selenium, and the electrochemical behaviors will be related to the surface character of the different samples.

Biomaterial Interfaces
Room Exhibit Hall C&D - Session BI-MoP

Biomaterial Interfaces Poster Session

BI-MoP4 Pulsed rf Plasma Polymer Modification of Microfluidic Devices*, **Z. Segu**,* Southern Illinois University*; R.B. Timmons,* University of Texas at Arlington*; G.R. Kinsel,* Southern Illinois University

There is a growing interest in the use of miniaturized systems - so-called "lab-on-a-chip" devices - for various analytical applications due to reduced solvent/reagent/sample consumption, shortened analysis time and the applicability of these devices to process / field analysis. One performance requirement for these devices often involves the ability to separate sometimes complex mixtures of analytes prior to detection. In conventional analytical instruments the separation step is most often achieved via gas or liquid chromatography using columns having a broad diversity of stationary phase chemistries. Introduction of similar diversity of chemistries into microfluidic devices can offer similar capabilities for complex analyte mixture separation while retaining the unique capabilities of the miniaturized system. In this research we explore the use of pulsed RF plasma polymer deposition for coating of channels in microfluidic devices. This approach to channel modification is attractive due to the conformal, sterile, pinhole-free, surface coverage of plasma polymer films and the wide variety of surface chemistries and functional group densities that can be achieved using RF plasma polymer deposition. In these initial studies RF plasma deposited microchannel polymer film coatings are investigated as a function of reactor power, monomer flow, monomer pressure, and positioning of the sample in the plasma reactor chamber. Resultant films are characterized by ellipsometry, SEM, FT-IR and XPS to determine various film properties including, film thickness, film uniformity and chemical functionality. These studies demonstrate the pulsed RF plasma polymer deposition can offer an effective means to incorporate a wide variety of chemical functionalities into microfluidic devices.

BI-MoP5 Pulsed RF Plasma-Modified Surfaces for On-Probe Fractionation and MALDI Mass Spectrometric Characterization of Bacterial Proteins*, **G.S. Fernando**,* Southern Illinois University Carbondale (SIUC)*; L.G. van Waasbergen, R.B. Timmons,* University of Texas at Arlington*; G.R. Kinsel,* Southern Illinois University Carbondale (SIUC)

Mass spectrometric characterization of bacteria is of growing importance, not only for applications in basic research but also as a means for rapid, unambiguous identification of bacterial pathogens. In this study, crude protein mixtures from cyanobacteria Synechocystis sp. strain PCC 6803 are characterized by Matrix-Assisted Laser Desorption Ionization Mass Spectrometry (MALDI-MS) following fractionation directly on the surface of pulsed RF plasma polymer modified On-Probe Affinity Capture (OPAC) MALDI probes. Pulsed RF plasma polymer deposition allows the incorporation of a wide diversity of surface chemistries and functional group densities directly on the surface of the OPAC MALDI probe, which can be subsequently used to selectively capture subpopulations of a complex protein mixture - for example, as derived from a bacterial source. OPAC protein mixture fractionation can be based on broad chemical properties (e.g. hydrophobic / hydrophilic, acid / base) or on highly bioselective interactions (e.g. metal binding properties, protein-substrate interactions). With careful optimization of the protein mixture deposition and washing procedures, fingerprint MALDI mass spectra of the bacteria proteome can be recorded which contain unique peptide and protein signature ions, not observed in the MALDI mass spectrum of the crude bacterial protein extract. The simplicity, speed and high sensitivity of the OPAC MALDI approach makes it an attractive option for bacterial proteome characterization.

BI-MoP6 Micropatterned Surface Modification of Polydimethylsiloxane via UV-Initiated Graft Polymerization of Acrylates*, **N. Patrito**, S. Chiang, P.R. Norton,* University of Western Ontario, Canada*; N.O. Petersen,* National Institute for Nanotechnology, Canada

Polydimethylsiloxane (PDMS) is a transparent, elastic polymer that is becoming an increasingly popular substrate for the fabrication of microfluidic devices. The widespread application of PDMS-based microfluidic devices to bioanalytical research has, however, been limited by the material's extreme hydrophobicity and surface inactivity. A desire to improve the wettability and biocompatibility of PDMS has resulted in a large body of research into the surface modification of siloxane polymers. One promising method for the permanent modification of PDMS is the covalent linkage of hydrophilic polymers on its surface via UV-initiated graft polymerization (UV-GP). Combining UV-GP with photolithographic techniques, poly(acrylic acid) and poly(methacrylic acid) patterns are successfully grafted onto PDMS thin films with micron-scale fidelity. Contact angle measurements, AFM imaging, surface roughness analyses, and XPS spectra confirm the presence of the grafted layers and provide insights into their morphology and surface coverage. This report also examines the effects of the graft materials on the adhesion and proliferation of common experimental cell lines, CV-1 and A-431. AFM images illustrate the improved attachment and growth of both cell types on the PAA and PMAA patterned substrates. These observations confirm the utility of UV-GP as a means of improving PDMS biocompatibility. They also demonstrate the amenability of the UV-GP technique to precise patterning, providing researchers with an effective, efficient means of localizing bio-adhesion on a variety of substrates.

BI-MoP7 Formation of Highly Oriented Hydroxyapatite Coating by rf Thermal Plasma Spraying*, **M. Inagaki**, Y. Yokogawa, T. Kameyama,* National Institute of Advanced Industrial Science and Technology (AIST), Japan

Hydroxyapatite (Ca@sub 10@[PO@sub 4@] @sub 6@ [OH] @sub 2@; HA) has been used for medical applications to promote the osteoconductivity of implanted materials.@footnote 1@ The HA crystal has hexagonal structure with space group of P63/m and has anisotropic properties of matter with respect to the crystallographic axis due to crystal structure of itself. Moreover, the HA crystal has two major surfaces i.e. (100) surface (a-surface) and (001) surface (c-surface) with different properties, such as protein absorption@footnote 2@ and dissolution behavior.@footnote 3@ In this study, highly oriented hydroxyapatite (HA) coatings were successfully obtained on titanium (Ti) substrates through a radio-frequency thermal plasma spraying method. XRD patterns showed that the HA coating layer had an apatite structure with (00l) preferred orientation vertical to the coating's surface. TEM observation showed that 200-800 nm-width prismatic crystals were formed in HA splats and the longitudinal axis of such prismatic crystals oriented vertical to the coating's surface. TEM images also indicate that the interface between prismatic crystals became compacted. SAD pattern show that the longitudinal axis of prismatic crystals corresponds to the (001) axis of HA. Protein absorption behavior of such a crystal oriented surface was also studied. @FootnoteText@ @footnote 1@ L. L. Hench, J. Am. Ceram. Soc., 81, (1998) 1705.@footnote 2@ T. Kawasaki, J. Chromatogr., 544, (1991) 147.@footnote 3@ H. Aoki, Surface Science, 10, (1989) 96.

BI-MoP8 Nanoscale Adhesion, Friction and Wear Studies of Biomolecules on Silicon Based Surfaces*, **D.R. Tokachichu**, B. Bhushan, M.T. Keener, S.C. Lee,* The Ohio State University

Protein layers are deployed over the surfaces of synthetic microdevices like bioimplants and bioMEMS to facilitate biocompatibility with biological tissue. When a biosensor comes in contact with any exterior environment like tissues, or fluids with a variable pH, the biomolecules on the sensor surface may get abraded due to a change in the adhesion between the biomolecules and microdevice surface. Friction and wear properties of biomolecules (e.g. proteins) on silicon based surfaces are important because these devices come across wear and friction when they are introduced into these environments. Changes in adhesion have been studied between streptavidin and a thermally grown silica substrate in phosphate buffered saline (PBS) solution with various pH values as a function of concentration of immobilized biomolecules in solution. Wear and friction properties of streptavidin (protein) biomolecules coated on silica by direct physical adsorption and chemical linker method were studied in PBS using tapping mode AFM at a range of free amplitude voltages.

BI-MoP9 Grafting of PEG-Macromonomers to Plasma Polymers Using Ceric Ion Initiation*, **N.J. Vickers,*** University of Sheffield, UK, United Kingdom*; A.G. Shard, S. Mac Neil,* University of Sheffield, UK

Bioadhesion, the adsorption of proteins, cells, or bacteria to a surface can be extremely detrimental to the performance of medical devices. Prevention of non-specific adsorption is therefore a key characteristic for many biomaterial applications and applying a non-fouling surface treatment can improve the performance of some medical devices. Poly(ethylene glycol) [PEG] is currently the most effective chemical modifier at reducing bioadhesion. Plasma polymers provide a thin, conformal base on which to graft. It is proposed that grafting PEG onto plasma polymers will confer non-fouling properties. Ceric ion initiation is commonly employed to graft polymers to natural polysaccharides e.g. starch. The initiation is thought to proceed through oxidation of hydroxyl groups. We have investigated ceric ion initiated grafting of PEG-macromonomers to several plasma polymers. Radio frequency glow discharge plasma polymerisation of isopropanol was carried out to obtain functional surfaces containing alcohol groups. Octadiene plasma polymer surfaces were made as a control hydrocarbon. Aqueous solutions of PEG-macromonomers and cerium ammonium nitrate were combined and plasma polymer samples introduced. Characterisation was carried out via X-ray photoelectron spectroscopy [XPS]. The influence of reagent concentration, chemical nature of the plasma polymer and grafting time were investigated. The success of ceric initiated grafting was demonstrated by the presence of a chemically shifted peak in the C1s narrow scan at 286.5eV binding energy. The intensity of this peak can be directly correlated with the amount of grafted material. Both time of reaction and concentration of initator have been shown to influence the polymer graft density, whilst the plasma polymer chemistry is of paramount importance. Currently work is underway to investigate the non-fouling properties of the PEG-grafted surfaces using protein adsorption methods.

BI-MoP10 SAM-Modification of Biomaterial Surfaces as an Antimicrobial Therapy*, **R.J. Emerson,** E.R. Soto-Villatoro, W.G. McGimpsey, T.A. Camesano,* Worcester Polytechnic Institute

Microbial infections of medical implants occur in more than 2 million surgical cases each year in the United States, increasing patient morbidity, mortality, cost and recovery time. While many methods exist to treat these infections, surgical excision of the infected device is the only certain cure. Clinically, it is of interest to determine the factors affecting microbial adhesion, the precursor to infection, and to formulate adhesion-resistant materials that are effective over protracted time periods. Self-assembled monolayers (SAMs) with a variety of terminal groups were developed and screened for antimicrobial activity. SAM molecules were bound to the surface using non-covalent metal-ligand bonds. The terminal groups of the surfaces included alkanethiols (C11 and C12), isophthalic acid (IPA), silver-containing isophthalic acid (IAG), bovine serum albumin (BSA), and tri-ethylene glycol (TEG). This methodology represents an advantage over physisorbed coatings and antimicrobial-impregnated implants, which may only prevent infection for short time periods, if at all. To screen the surfaces, single, viable bacterial cells (Staphylococcus epidermidis, Clinical isolates) were chemisorbed to the silicon cantilever of an atomic force microscope (AFM) probe, and brought into contact with the SAM surfaces. Force profiles were measured for approach and retraction interactions. IPA and IAG coatings showed promising results, since they demonstrated the lowest adhesion forces for the S. epidermidis probe.

BI-MoP11 The Effect of Solid Surface Tension on Biofilm Adhesion*, **R.A. Brizzolara,** R.M. Lennen,* NSWC, Carderock Division

The effect of material properties on the biofouling of a surface is of great practical importance. Biofouling is a chronic and costly problem in the maritime industry as well as being a significant issue for the medical community. This study investigates the effect of solid surface tension on microbial biofilm adhesion and accumulation. The experimental approach was designed to isolate the effects of solid surface tension on the biofilm from the effects of other material properties such as elastic modulus and surface topography, as well as to isolate biofilm accumulation from biofilm adhesion. Covalently bound monolayers of organosilanes were prepared on native titanium oxide surfaces. The solid surface tension was varied through the choice of the terminal group, using hexadecyltrichlorosilane, 1H,1H,2H,2H-perfluorooctyltrichlorosilane and 3-chloropropyltrichlorosilane precursors. This resulted in surfaces with a wide range of solid surface tensions, while retaining the original topography and modulus. Monolayer deposition was verified using contact angle/solid surface tension measurements and x-ray photoelectron spectroscopy (XPS). Biofilm accumulation and adhesion measurements were performed by growing Pseudomonas fluorescens biofilms under gentle agitation (~120 RPM shaker) and performing a Bradford protein assay before and after exposing the coupons to hydrodynamic shear stresses of 3.7 N m-1 in a turbulent flow cell. It is expected that the results of this study will assist in the design of advanced coatings and surfaces by defining the optimum solid surface tension for reduced biofouling. This work was funded by the NSWC, Carderock Division In-House Laboratory Independent Research (ILIR) program.

BI-MoP13 Controlled Release of Calixarenes from Chitosan Hydrogel Coated Polymeric Surfaces as Antimicrobial Treatment of Staphylococcal Infections*, M. Vinante, C. Pederzolli, L. Pasquardini, L. Lunelli, **R. Canteri**, M. Anderle,* ITC-irst, Italy*; C. Potrich, G. Viero, M. Dalla Serra,* CNR ITC, Italy*; G. Prevost, O. Joubert,* Institut de Bactériologie de la Faculté de Médecine, France

The proliferation of pathogenic microorganisms on biomaterial surfaces is one of the most widespread causes of failure of biomedical devices such as catheters, medical implants, vascular graft and joint prostheses. Staphylococcus species (e.g. aureus and epidermidis) are one of the major pathogens isolated in hospitals and are responsible for numerous nosocomial infections. Common virulence factors of these pathogenic staphylococcal strains are a group of secreted leucotoxins, which belong to the family of @beta@-barrel pore-forming toxins. They form poorly selective holes into the membrane of attacked cells, causing their lysis. We developed a local drug delivery system composed of chitosan hydrogel deposited on polymeric surfaces and loaded with hydrophilic agents, calixarenes. These molecules have been demonstrated to have an inhibitory effect on leucotoxins during pore-formation (reduction of 50% of hemolytic activity of 12 nM HlgA/HlgB on HRBC using 6 µmM of 4-sulfonic-calix(6)arene). Two different strategies of hydrogel formation are evaluated, one based upon ionic interactions between positively charged groups of chitosan chains and negative charges of calixarene molecules; the latter utilizing an homofunctional derivative polyethylene glycole as cross-linking agent (e.g. ButyrALD-PEG-ButyrALD) in order to form a permanent network with enhanced mechanical properties. These two kinds of interactions were also employed to stabilize the hydrogel film to the substrate. Data on the physical-chemical and morphological properties of the chitosan deposited hydrogel and the kinetics of calixarene release will be presented. @FootnoteText@ @footnote 1@Work supported by the P.A.T. Trento- Italy- Fondo Unico (project StaWars).

BI-MoP14 The Effect of Covalent Tethering on the Function of a Quaternary Ammonium Antimicrobial Compound*, R.A. Brizzolara, **D.M. Stamper,** R.M. Lennen,* NSWC, Carderock Division

In the development of antimicrobial coatings and materials, biocidal molecules can be incorporated into a coating either as free molecules, or by covalently tethering the molecules to the coating or surface. Covalently tethering a biocidal moiety to a coating or surface has the benefit of reducing leaching of the biocide into the environment. However, the effects of covalent tethering on the biocidal activity of the molecule need to be more fully characterized. This paper reports on experiments to determine the effects of surface-immobilization on the activity of an antimicrobial molecule. Monolayers of a covalently bound organosilane containing a quaternary ammonium functional group (QAS) were used as the test platform. QAS monolayers were bound to silica surfaces and characterized by x-ray photoelectron spectroscopy (XPS). Viability of Staphylococcus aureus exposed to QAS-derivatized surfaces was measured by dilution plate counting. Control substrates derivitized with an amino-terminated silane were also included in the analysis. Flat surfaces derivatized with QAS did not possess antimicrobial activity. Results will be presented that differentiate between 1. loss of biocidal activity as a result of covalent tethering of QAS molecules versus 2. insufficient dose of antimicrobial molecules per S. aureus cell, as the cause of lack of antimicrobial activity of QAS-derivatized surfaces. It is expected this work will contribute to the development of materials and coatings with inherent antimicrobial properties and to reduced use of decontaminating solutions containing toxic chemicals. This work was funded by the NSWC, Carderock Division In-House Laboratory Independent Research (ILIR) program.

BI-MoP15 Protein Adsorption on Poly(Ethylene Glycol)-Modified Surfaces under Flow Conditions in Microfluidics Systems, ***C.J. Chun***, *K. Lenghaus,* University of Central Florida*; D.C. Henry,* Clemson University*; L. Riedel, A. Bhalkikar, J.J. Hickman,* University of Central Florida

In the last decade microfabrication technology has been used to create new microfluidics systems, bioanalytical and medical devices. The handling of relatively small amounts of analytes, at significantly lower concentrations, combined with the fact that the surface-to-volume ratio increases in direct proportion to the device size decreasing, could create potential problems in device utilization. The problem being that, the analytes or target molecules may be completely non-specifically adsorbed on the surfaces of the microdevices before they reach the detector. Thus, the basic understanding of an adsorption behavior of biomolecules@footnote 1@ on the surfaces of these systems is critical for their use in microfluidics as well as bioanalytical devices. To investigate the situation we have developed assays@footnote 2@ to evaluate protein adsorption under flow and static conditions at submonolayer coverages on poly(ethylene glycol) (PEG)-modified surfaces, which are well known to resist protein adsorption.@footnote 3@ In this study, protein adsorption onto PEG-modified microcapillary surfaces, under flow conditions, has been determined at different flow rates as well as various protein concentrations. Alkaline phosphatase and horseradish peroxidase were used to evaluate proteins adsorption behavior, which although low, was still significant. The flow rate was also seen to affect the protein adsorption on the PEG-modified-surfaces. Simulation studies of the protein adsorption behavior are also being used to help in the development of new biocompatible microfluidics systems.@footnote 4@. @FootnoteText@ @footnote 1@K. Nakanishi, T. Sakiyama, and K. Imamura, J.Biosci.Bioeng., 91, 233 (2001). @footnote 2@K. Lenghaus, J.W. Dale, J.C. Henderson, D.C. Henry, E.R. Loghin, and J.J. Hickman, Langmuir, 19, 5971 (2003). @footnote 3@M. Zhang, T. Desai, and M. Ferrari, Biomaterials, 19, 953 (1998). @footnote 4@J. Jenkins, B. Prabhakarpandian, K. Lenghaus, J.J. Hickman, and S. Sundaram, Anal.Biochem., 331, 207 (2004).

BI-MoP16 Materials Characterization for Blood-Flow Dynamics and Platelet-Adhesion Simulation of Hematocompatible Plasma-Polymerized Tetraglyme Surfaces, ***E. Hanley***, *J.L. Shohet, J.L. Lauer, R.M. Albrecht, S. Esnault, J.S. Malter, R.H. Blick, H.S. Kim,* University of Wisconsin-Madison*; U. von Andrian,* Harvard Medical School*; S.B. Shohet,* University of California, San Francisco

The realization of small-scale biomedical devices will be closely related to the non-fouling/biocompatible properties of the exposed surfaces and the uniformity of the surface treatment throughout the device. Thrombus formation and embolization are significant problems for blood-contacting biomedical devices which often begin with platelet adhesion. In this work, we explore plasma polymerization (PP) to improve the hematocompatibility of silicon-based surfaces and the process conditions necessary to develop a uniform PP coating on the lumenal surface of artificial blood vessels. To minimize these effects, plasma-polymerized tetraglyme was deposited on flat Si@sub 3@N@sub 4@ and SiO@sub 2@ samples to produce a PEO-like surface coating. The dynamics of platelets can be modeled using a numerical simulation of adhesive particles interacting with an adhesive surface.@footnote 1@ Experimentally, emitted light from the plasma during the PP process was fed into a monochromator. Coating thickness and chemical composition of the surfaces was measured using ellipsometry and XPS, respectively. Contact-angle measurements were carried out on the PP surfaces. An atomic force microscope was used to determine the surface topology of the coated PP surface. To test platelet adhesion, the PP surfaces were exposed to heparinized human blood. After blood exposure, a scanning electron microscope was utilized to assess the density of adhering platelets on the PP surfaces. The plasma-treated surfaces showed fewer blood adherents than the untreated surfaces. The simulation can include the surface topology as measured by the AFM. By suitably modifying the plasma parameters, the plasma-polymerization treatment can be optimized with the eventual goal of producing biocompatible, small-diameter (< 5 mm ID) artificial blood vessels that contain integrated sensor systems. @FootnoteText@ @footnote 1@M.R. King and D.A. Hammer, Biophys. J. v.81, 799-813 (2001).

BI-MoP17 Studies of Protein Interactions with CaP Surfaces Using XPS and ToF-SIMS, *C. Mendoza-Barrera, H.E. Canavan, R. Michel,* ***D.G. Castner***, University of Washington

Proteins directly control the nucleation and growth of biominerals, but the details of molecular recognition at the protein-biomineral interface remain poorly understood. The elucidation of recognition mechanisms at this interface may provide design principles for advanced materials development in bone replacement. In this work, we characterize the interactions of proteins with the principal calcium phosphate components of bone. Using X-ray diffraction (XRD), we characterized the purity and phases of hydroxyapatite (HAp), dibasic calcium phosphate dihydrate (DCPD), dibasic calcium phosphate (DCP), @beta@ tribasic calcium phosphate (@beta@-TCP) and monbasic calcium phosphate (MCP). Next, adsorption isotherms of different proteins (e.g. BSA and fibrinogen) were performed on each calcium phosphate substrate. In this way, the solution concentrations necessary to produce sub-monolayer and monolayer thicknesses of each protei n was determined via X-ray photoelectron spectroscopy (XPS). As the conformation of proteins is greatly influenced by their density on a surface, we next used time-of-flight secondary ion mass spectrometry (ToF-SIMS) to compare the comformation of different protein layers adsorbed on the different calcium phosphate substrates. Finally, we discuss the effect of protein identity, conformation, and the character of the calcium phosphate substrate have on protein adsorption.

BI-MoP18 Syntheses of Polymer-Protein Composites by Plasma-Spinning Deposition, ***R. Ohta***, *N. Saito, O. Takai,* Nagoya University, Japan

Blood and/or tissue contacting biomaterials as catheters, artificial blood vessels and artificial valves are desired to have higher biocompatibilities in the medical field. Therefore, polymer-protein composites, which are expected to have excellent biocompatible surfaces, have been attracting attentions of many researchers. In this research, we aimed to synthesize polymer-protein composites by plasma-spinning deposition (PSD). In the PSD, the polymer composites were synthesized from precursor solutions. The precursor solutions were filled in a metallic capillary tube. Plasma were produced by applying voltages to the capillary tube. The polymer composites were synthesized on substrates from the precursors, which passed through the plasma. Two different processes were examined to synthesize the polymer-protein composites: (i) PSD of the polymer-protein composites from mixed solvents of the precursor polymers and proteins, and (ii) immobilization of proteins to the polymers synthesized by the PSD. Polyethylene terephthalate (PET), polyurethane (PU) and polyacrylonitrile (PAN) were used as precursor polymers. Proteins as fibrinogen, heparin and albumin were contained into the polymer composites. The PSD process was optimized by varying the concentrations of the polymers and proteins in the precursor solutions and by controlling the plasma states during the PSD. The chemical structures of the polymer-protein composites were analyzed by spectroscopic methods as X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy (RS), etc. The surface characteristics of the polymer-protein composites were investigated by scanning electron microscope (SEM), atomic force microscope (AFM), etc.

BI-MoP19 Alginate Adsorption to Charged Surfaces: The Importance of Protein Co-Adsorption, ***N. Chandhok***, *K.T. Queeney,* Smith College

The adhesion of extracellular bioploymers, including polysaccharides and proteins, to solid surfaces is a critical step in biofilm formation. It has been shown previously that alginate, a charged polysaccharide, will adhere to amine-terminated surfaces,@footnote 1@ and that the presence of a protein conditioning film can enhance alginate adsorption.@footnote 2@ We have used surface infrared spectroscopy to examine the adsorption behavior of alginate and find that protein co-adsorption is in fact essential for adhesion of this negatively charged polymer even to positively-charged surfaces. Specifically, the co-adsorption of protein impurities, which are present in quantities less than 50 ng/mL, is seen in all cases of alginate adsorption. When these impurities are filtered out by adsorption to high surface area MgO, no alginate adsorption is detected. Exposure of purified alginate solutions to protein conditioning films prepared from specific, known proteins is used to identify the critical polysaccharide/protein interactions that favor biofilm formation. @FootnoteText@ @footnote 1@R. Dhamodharan and T. J. McCarthy, Macromolecules 1999, 32, 4106-4112.@footnote 2@P. A. Suci and G. G. Geesey, J. Coll. Interface Sci. 1995, 172, 347-357.

BI-MoP21 Prediction of Protein-Surface Interactions by All-Atom Molecular Dynamics Simulations Using Implicit Solvation, ***Y. Sun***, *F. Wang, R.A. Latour,* Clemson University

The orientations and conformations of adsorbed proteins on biomaterials surfaces have profound influences on their bioactivities. However, it's very difficult to resolve the structures of adsorbed proteins experimentally. Empirical force field-based molecular simulation can be used to complement experimental studies to investigate protein adsorption behavior and potentially provide a more detailed understanding of molecular-level interactions. The predictive power of such an approach is largely dependent on the accuracy of the underlying force field used and the adequacy of sampling in the simulation. The objective of this study is thus to develop an empirical force field method with enhanced sampling to enable protein adsorption to be accurately simulated. We are evaluating the use of a generalized Born-based analytical continuum electrostatics (ACE) implicit solvent model for the purpose of enabling protein adsorption to be simulated with solvation effects treated implicitly. To further enhance sampling, replica-exchange molecular dynamics (REMD) is employed in combination with ACE to predict the equilibrium structures of a model protein (lysozyme) on alkanethiol self-assembled monolayer (SAM) surfaces. We have determined that ACE predicts reasonable energy-distance relationships of mid-chain peptide residues on functionalized SAM surfaces; it also predicts reasonable and stable trajectories of native lysozyme structure and significant surface-induced conformational changes of lysozyme on SAM surfaces. Qualitative agreement between model predictions and experimental observations has been established, and further studies for model validation are planned.

BI-MoP22 Role of the Chemical and Morphological Surface Properties in Platelet Binding and Protein Adsorption to Biomaterial Surfaces*, S. Forti, M. Vinante, L. Pasquardini, L. Lunelli, L. Vanzetti, R. Canteri, C. Pederzolli,* ***M. Anderle****,* ITC-irst, Italy*; S. Pascale,* Sorin Biomedica Cardio S.p.A, Saluggia (VC), Italy*; G. Rossetti,* S. Chiara Hospital, Italy

Many existing medical implants are associated with poor interfacial biocompatibility. An example is represented by the cardiovascular devices; their implantation induces a complex blood-material interaction, often leading to thrombus formation. This work describes the characterization of the protein layer and the process of platelets adhesion on four different materials (Sorin pyrolytic carbon (PyC), two different types of polystyrene and titanium alloy) after contact with human platelet poor plasma and platelet rich plasma in static conditions. Total protein quantification on eluted samples revealed that PyC adsorbed the lowest amount of plasma proteins. Using immunofluorescence microscopy specific proteins promoting platelets adhesion were characterized on PyC and titanium alloy: fibronectin was found to be present at very low levels on both surfaces while fibrinogen and von Willebrand factor adhered to PyC in a higher proportion. Adherent platelets and shape categories distribution were quantified using scanning electron microscopy (SEM) and atomic force microscopy (AFM). PyC induced less adhesion with mostly weak activated platelets, however aggregates may be present. Titanium alloy promoted a higher adhesion, with more active platelets but less cohesive. Polystyrene materials were almost covered by spread platelets. Material surface properties were evaluated by contact angle, electron spectroscopy for chemical analysis (ESCA), secondary ion mass spectrometry (SIMS) and atomic force microscopy (AFM). The final goal will be to correlate the biological response with surface morphological and physico-chemical properties of the materials.@footnote 1@ @FootnoteText@ @footnote 1@Supported by the Provincia Autonoma di Trento, post-doc project Emosurf and by National Department of Health.

BI-MoP23 Adsorption of Human Serum Albumin on Carbon Nitride Films Studied with in-situ Ellipsometry*,* ***T. Berlind****, M. Poksinski, L. Hultman, P. Tengvall, H. Arwin,* Linköping University, Sweden

Carbon based materials have received considerable attention during the last decades due to their interesting tribological, electronic and optical properties. So far not much effort has been put into the investigation of the use of these materials in biotechnology. The objective with this study is to investigate the interaction of carbon and carbon nitride surfaces with proteins. Carbon nitride (CN@sub x@) and amorphous carbon (a-C) thin films were deposited on silicon substrates by reactive sputtering. By changing sputtering parameters the microstructure can be controlled and amorphous, graphitic and fullerene-like films were grown to a thickness of 200 nm. Prior to protein adsorption, the three structures of CN@sub x@ films and the a-C films were optically characterized with spectroscopic ellipsometry in the wavelength range 350-1700 nm and with infrared ellipsometry in the range 2-30 µm to determine their complex-valued refractive index N=n+ik. Contact angles for the films were measured with water. The films were exposed to human serum albumin and the adsorption was monitored in-situ using dynamic ellipsometry. From the ellipsometric data the adsorbed amount of proteins was quantified in terms of surface mass density using de Feijters model. The protein layer index was described with a Cauchy model. The results indicate larger adsorption of protein onto the amorphous films compared to the films with more ordered structure.

BI-MoP24 Infrared Spectra of Serum Albumin Immobilized in Porous Alumina*,* ***L.G. Castro****, S. Sarkar, D.W. Thompson, J.A. Woollam,* University of Nebraska-Lincoln

While most studies of protein-surface interactions rely on chemistry to obtain specific information about what proteins are present, infrared absorption spectra also contain protein-specific features. Reliable measurement of these spectra could, for example, help identify nonspecific binding. Here porous alumina was used as a capture matrix to increase the detectability of protein infrared spectra. Layers of porous alumina were fabricated electrochemically and fully characterized using visible and mid-infrared (mid-IR) spectroscopic ellipsometry (SE). Pore sizes and center-to-center spacings were engineered to efficiently capture human serum albumin (HSA). The layers were exposed to solutions of HSA in an acetate buffer. The incorporation of the proteins into the matrix was monitored by multiwavelength visible SE. The samples were characterized before and after protein attachment with mid-IR SE. A methodology was developed to obtain the infrared dielectric function @epsilon@ of the adsorbed proteins. Full optical modelling was essential to separate the protein peak signatures from those of the alumina. Strategies to improve capture efficiency and reduce uncertainty of the @epsilon@ spectrum are discussed.

BI-MoP25 Vacuum UV to Mid-Infrared Optical Study of Immunoglobulin G Attachment to Chemical Modifications of Chitosan*,* ***W.H. Nosal****, S. Sarkar, D.W. Thompson, A. Subramanian, J.A. Woollam,* University of Nebraska-Lincoln

Optical constants of spin-cast chitosan films were determined from vacuum-ultraviolet (VUV) to mid-infrared (130 nm to 30 microns). Both pure and chemically modified chitosan films were studied using spectroscopic ellipsometry (SE). Chemical modification by attachment to the amine group in chitosan was performed using 1,2 Epoxy-3-phenoxy-propane, commonly known as glycidyl phenyl ether (GPE), to produce a hydrophobic surface. A similar modification with succinic anhydride yields a hydrophilic surface. Quantitative lineshape analysis of the optical constant spectra was performed using Lorentzian and Gaussian line-shapes, including anisotropic response due to molecular-bond orientations in-plane and out-of-plane. Dynamic in situ visible SE has been used to study the attachment of immunoglobulin G to each modified surface type (hydrophobic/hydrophilic), followed by VUV to mid-infrared ex situ SE optical analysis. Research supported by U. S. Army contract # W911NF-04-2-0011, and the College of Engineering, University of Nebraska.

BI-MoP26 Effects of Fluorescent Dyes on the Structure of Lipid Membranes*,* ***J.J. Heetderks****, P.S. Weiss,* Penn State University

Cell membranes are complex, dynamic mixtures of lipids, proteins, and cholesterol; their precise mode of molecular organization is unknown. Transient associations of molecules form â?olipid raftsâ?⍰ in active cells that may affect membrane-associated protein activity. One model to study the lipid component of these molecular interactions is the giant unilamellar vesicle (GUV). The lipids, without contribution from membrane proteins, cytoskeletal structures, cholesterol, or outside forces, form domains in GUVs when the conditions are within an appropriate range of the multi-dimensional phase diagram of lipid composition and temperature. Fluorescently labeled phospholipids and lipid analogues are used at low concentrations to visualize the vesicles and domains, and are found to influence measured membrane properties, even at concentrations below those typically used in structural studies. Through basic membrane organization measurements, we determine the effects on the vesicle properties for which the labeling is responsible. We incorporate varying amounts of fluorescent dyes into 2-phase vesicles and find clear divisions of gel and fluid domains at room temperature. The temperature is then slowly raised while monitoring the membrane domains until the domains melt into one homogeneous phase. Preliminary results show that the incorporation of several common fluorescent labels in the membrane cause measurable changes in the demixing temperatures of the two-phase vesicles at less than one percent dye concentration.

BI-MoP27 Cell Adhesion of Plasma Polymerized Allylamine Coating on Polymeric Substrates*,* ***S.R. Kim****,* Chungju National University, South Korea

RF plasma enhanced chemical deposition was used to get biocompatible coating on polymeric substrates with various processing conditions, such as input power, monomer/oxygen feed ratio, modulated frequency and duty cycle. Allylamine was used as feed monomer and oxygen was used as mixing gas. Input power was varied from 50 to 300 Watt. Deposition rate was 16 nm/min. Chemical bonding information of deposited film by FTIR-ATR showed peak broadening compared to the allylamine monomer and

C=N stretching peak near 2200 cm@super -1@ appeared for polymerized coating. Contact angle was changed from 88° for untreated polystyrene to 30° for treated polystyrene without oxygen input. Contact angle of plasma polymerized allylamine coating obtained with oxygen input was 8°. Untreated polystyrene film had rough surfaces and the average roughness was 10.91 nm, however, the plasma coating deposited polystyrene with introduction of oxygen, the roughness decreased to 3.91 nm and it decreased to 1.98 nm without oxygen input. ESCA showed N/C ratio of 13.4, 4.36 for samples prepared with oxygen input and without oxygen, respectively. Fibroblast cell was used and MTT assay was done. Cell viability 4 days after seeding was decreased as amount of oxygen increased.

BI-MoP28 Controlled Passive Transport through a Cellular Mimetic Membrane Consisting of a Stochastic Array of SiO2-coated Vertically Aligned Carbon Nanofibers*, **J.D. Fowlkes,*** The University of Tennessee, Knoxville, US*; B.L. Fletcher, E.D. Hullander, M.L. Simpson, A.V. Melechko,* The University of Tennessee, Knoxville*; M.J. Doktycz,* Oak Ridge National Laboratory

A cell mimic device has been fabricated for the purpose of mimicking and interfacing to biological processes at the molecular scale. The design of the device addresses the challenge of fabricating and filling small physical volume enclosed membrane structures. The device has the additional advantage of being totally synthetic. The feasibility of using vertically aligned carbon nanofibers (VACNF) as the semi-permeable membrane component of the cell mimic device has been successfully verified by demonstrating the controlled and size-selective transport of nanoscale species by the VACNF membrane. To date, the controlled delivery and containment of picoliter volumes to individual cells has been achieved and the efficacy of the semi-permeable membrane component of the cell mimic to mediate passive diffusion transport has been evaluated. We report here the identification of discrete regimes of membrane transport behavior based on the ability to tailor nanoscale aspects of the membrane pore by controlled oxide deposition. VACNF based membrane elements that are stochastically prepared exhibit a strong statistical nature on the nanoscale. Stochastic features are preferable over patterned ones in terms of reduced fabrication complexity but exhibit statistical deviations that lead to properties that are difficult to predict. We have created a Monte Carlo based simulation to replicate and simulate the stochastic nature of the VACNF membrane and the passive diffusion through the membrane, respectively. The simulation was found to correlate strongly with experimental results. These predictive capabilities help facilitate device design and reduce the number of experimental characterizations. Further, the results reported here implicate stochastic, statistical nanoscale structures as realistic components in integrated devices with stringent requirements on discrete and reproducible behavior.

BI-MoP29 Calcium Ion Free Supported Lipid Bilayer Formation by Giant Vesicle Fusions*, **Y.-H. Kim**, Md. Rahman,* The Graduate University for Advanced Studies, Japan*; R. Tero, T. Urisu,* Institute for Molecular Science , NINS, Japan

Supported membranes are the lipid bilayers supported on the solid substrate, which are commonly used as a model membrane for the in vitro study of the fundamental properties of biological membranes and various biotechnological applications. We have investigated the effect of the electrostatic attractive force between vesicles and the surface on the supported lipid bilayer formation using atomic force microscopy (AFM) and fluorescence microscopy. In most of the lipid bilayer formation by vesicle fusion, Ca@super 2+@ are added to the vesicle suspensions to induce the rupture of the vesicle. The lipid bilayer formation under the Ca@super 2+@ free is required in such cases of the study of Ca@super 2+@ effects on the membrane surface reactions. When the bare SiO@sub 2@ surface was incubated in the suspension of the negatively charged giant vesicle without Ca@super 2+@, extremely low surface coverage of lipid bilayer was observed due to the surface-vesicle charge repulsion. while, high coverage of lipid bilayer was observed when Ca@super 2+@(final concentration 5 mM) was added before incubation. The remarkable difference in the coverage of the lipid bilayer on the SiO@sub 2@ surface according to the existence of calcium ion can be explained in terms of the adsorption of giant vesicles. As to the formation of the lipid bilayer, the adsorption is the initial step, and therefore a stable and strong adsorption is necessary to form high coverage of the lipid bilayer. In case of the positively charged surface modified by Aminoproplydimethylethoxysilane, the high surface coverage of the lipid bilayer was obtained without adding Ca@super 2+@. The strong electrostatic attractive force between vesicles and the surface of opposite charge enhances the stable adsorption of negatively charged giant vesicles, which promotes the lipid bilayer formation. The control of the surface and the vesicle charge is an important factor to make a supported lipid bilayer without calcium ion.

BI-MoP30 ToF-SIMS Chemical Imaging Analysis of Micropatterned Streptavidin and Cells without Labeling*, **T.G. Lee,*** Korea Research Institute of Standards and Science (KRISS), Korea*; H.K. Shon,* Korea Research Institute of Standards and Science (KRISS)*; K.-B. Lee,* Korea Advanced Institute Science and Technology (KAIST)*; J. Kim,* Sungkyunkwan University, Korea*; J.C. Lee,* Samsung Advanced Institute of Technology (SAIT), Korea*; I.S. Choi,* Korea Advanced Institute Science and Technology (KAIST)*; D.W. Moon,* Korea Research Institute of Standards and Science (KRISS)

In this work, three different analysis ion beams (Ga@super +@, Au@super +@ and Au@sub 3@@super +@) were used to obtain label-free time-of-flight secondary ion mass spectrometry (ToF-SIMS) chemical images of microcontact printed streptavidin. The image of total ions obtained by an Au@sub 3@@super +@ primary ion beam corresponded well to the real image of micropatterned streptavidin, whereas the total-ions image by Ga@super +@ or Au@super +@ primary ion beams did not. A principal component analysis (PCA) of ToF-SIMS data was initially performed to identify characteristic secondary ions of streptavidin. Chemical images of each characteristic ion were reconstructed from raw data and used for the 2nd PCA run, which resulted in a contrasted, and corrected, image of micropatterned streptavidin by Ga@super +@ and Au@super +@ ion beams. This suggests that ToF-SIMS imaging along with multivariate data analysis would be an effectual method of obtaining label-free chemical images of patterned proteins or biomolecules. Label-free chemical images of micropatterned A431 cells were obtained by using the same procedure.

BI-MoP31 Effects of Surface Topography, Chemistry and Wettability on Osteoblast Cell Adhesion and Mineralization on Sol-Gel-Derived Titanium Alloy*, **M.C. Advincula**, E.T. Ada, F.G. Rahemtulla,* University of Alabama at Birmingham*; R.C. Advincula,* University of Houston*; S.L. Bellis, J.E. Lemons,* University of Alabama at Birmingham

The biological events occurring at the bone-implant interface are influenced by the topography, chemistry and wettability of the implant surface.The surface properties of titanium alloy Ti6Al4V prepared by surface sol-gel processing (SSP) were investigated systematically using x-ray photoelectron spectroscopy, scanning electron microscopy, atomic force microscopy and contact angle metrology. Biocompatibility of the oxide was assessed by evaluating MC3T3 osteoblastic cell adhesion to the substrate, as well as by matrix mineralization. The sol-gel coated surface had predominantly a TiO@sub 2@ composition with abundant hydroxyl OH- groups, and was highly wettable, with increased roughness and porosity. Significantly more cells adhered to the sol-gel, as compared with passivated surfaces, at 1 and 24 hours following cell seeding, and a markedly greater number of bone nodules were observed on sol gel coatings. Favorable cellular responses were attributed to the rougher porous surface, hydrophilicity and increased hydroxyl group content of the sol gel, properties which, in turn, are known to regulate the adsorption of pro-adhesive serum proteins onto material surfaces.Collectively our results show that surface properties of titanium alloy can be modified by SSP to further enhance the bioactivity of this biomaterial.

BI-MoP33 Electrical Monitoring of Cell Interaction on a Microelectronic Interface*, H.D. Wanzenboeck, **K. Dominizi**, P. Hagl, E. Bertagnolli,* Vienna University of Technology, Austria*; E. Bogner, F. Gabor, M. Wirth,* University Vienna, Austria

*****PLEASE NOTE: YOU MUST IDENTIFY A DIFFERENT PRESENTER FOR THIS ABSTRACT. YOU MAY ONLY PRESENT ONE (1) PAPER AT THE CONFERENCE*****The electrical measurement of tissue properties and of cell signals has gained increased interest for ceel-based biosensor applications in medicine, pharmacology and biology. Yet, the interaction of living cells on solid sensor surfaces has not been thoroughly investigated. For application mainly microelectronic sensors are attractive due to the small size and the low cost in mass production. The objective of this work was to investigate the interaction of living human cells with microelectronic surfaces. We have performed a comprehensive study of the cells behaviour on semiconductors, metals and dielectric materials commonly used in microelectronics. Human ephitelal cells (Caco-2) were grown in-vitro on the surface of the microelectronic substrates. In a second step we have systematically varied the geometry of the surface by etching trenches with a width from 2 up to 60 µm and a depth of 2 to 30 µm into a biocompatible substrate. The growth of ephitelial cells on flat and on ridged surfaces was compared. The response of the cell behaviour on the varying surface was investigated by optical, electronoptical, enzymatic and biochemical methods. The effects of surface alterations on the proliferation rate, the cell adhesion, the cell coverage and the differentiation of cells was investigated. Finally, a microelectrode structure with microelectrodes (2x2 µm2) smaller than a single cell was implemented on the previously investigated surfaces. The electrical properties of the cell layer and of single cells could be evaluated by impedance spectroscopy. Differences of the impedance were monitored during progressing aging of cells. The interpretation of the interrelated analysis results shines a new light on the interaction of living cells with sensor interfaces. The feasibility to identify changes of the cell-surface interaction by electrical measurements was successfully demonstrated.

BI-MoP35 Fabrication of a Polyallylamine-Based, Label-Free Piezoelectric Biosensor Platform*, A. Papadopoulou-Bouraoui,* *F. Bretagnol, M. Lejeune, A. Valsesia, J. Barrero-Moreno, D. Gilliland, G. Ceccone, F. Rossi,* European Commission-Joint Research Centre, Italy

The Quartz-Crystal Microbalance (QCM) is a sensitive acoustic technique allowing the measurement of resonance frequency changes occurring due to changes in the total oscillating mass of the crystal. It operates as a highly sensitive weighing device. The aim of the present study was to use active amino groups provided through plasma deposition of an allylamine polymer film (PALL) towards further antibody immobilization. Two antibody immobilization routes were investigated. The first involved the use of glutaraldehyde as a crosslinker, followed by protein A (PA) or protein G (PG) for optimal antibody orientation and consecutively highly sensitive antibody-antigen interaction. The second involved the use nanometer-sized gold (20 nm) particles in combination with PA or PG. PALL films were deposited in a capacitively coupled plasma reactor onto the SiO2 covered surface of the quartz crystal and were completely characterized before antibody immobilisation. The active amino groups were quantified through evaluation of the X-Ray Photoelectron Spectroscopy (XPS) C1S high-resolution spectra of the trifluoromethylbenzaldehyde derivative. Evaluation of the stability and reactivity of all main intermediate steps was performed using the QCM in combination with other surface characterization techniques such as the Ellipsometry, Atomic Force Microscopy (AFM), Time-of-Flight Secondary Ion Mass Spectrometry and XPS. Results from this work show the possibility of producing simple, direct piezoelectric immunoprobes through appropriate antibody orientation, using PA or PG, or surface increase, using GNP, without the need for labeled compounds. The combination of surface analytical, optical and mass balance techniques is confirming the effectiveness of these immunosensor fabrication strategies. This fully characterized biosensor platform has been tested for the detection of a food allergen, ovalbumin.

BI-MoP36 Formation of Carbohydrate Microarrays with the MAPL Technique for the Detection of Specific Interactions*, K. Barth,* *G. Coullerez, M. Textor,* ETH Zurich, Switzerland

Carbohydrates play an important role in many biological processes, like cell-cell and cell-pathogen recognition.@footnote 1@ Because of missing analytic tools there is until now little known about the role of carbohydrates in these processes. Therefore it exists a need for methods that allow high throughput screening of these specific interactions.@footnote 2@ We have newly developed a method to covalently graft mono-, di- and trimannosides to the polycationic copolymer poly(L-lysine)-graft-poly(ethylene glycol) (PLL-[g]-PEG). With this system it is possible to tailor the density and distribution of the immobilized mannosides on the polymer backbone. While spontaneously adsorbed on negatively charged oxides surfaces (Nb @sub 2@O@sub 5@, TiO@sub 2@) the copolymers show specific lectin and bacteria recognition. Furthermore we could demonstrate the dependence of the carbohydrate surface density for the interactions between the mannoside and the multivalent model systems Concanavalin A (Con A) or Escherichia coli (E. coli). This was done with methods like Optical Waveguide Lightmode Spectroscopy where no additional labeling is required. In order to develop arrays, we propose herein to combine this chemical approach with the patterning method MAPL (Molecular assembly pattering by lift-off) developed by Falconnet et al.@footnote 3@ This technique combines photolithography and the attribute of functionalized PLL-[g]-PEG to form uniform layers on many metal oxide surfaces. We are able to control the pattern geometry and size as well as the surface density of the mannosides in the adhesive patterns. Fluorescent labeled Con A and E. coli can be easily detected and is proofing the high specificity of the developed system with a non fouling background. @FootnoteText@ @footnote 1@ Sharon et al., Sci. Am. 1993, 268, 82.@footnote 2@ Seeberger et al., ChemBioChem 2004, 5, 1375.@footnote 3@ Falconnet et al., Nano Letters, 2004, 4, 1909.

BI-MoP37 Combinatorial Characterization of Geometric Effects on the Optical Properties of Gold Nanostructures for Biosensors Optimization*, G. Nusz,* *A. Curry, A. Wax, A. Chilkoti,* Duke University

Optimizing the performance of nanoparticle optical biosensors requires design of nanostructures that exhibit the greatest change in their extinction spectrum upon receptor-analyte binding. Previous studies have suggested that highly anisotropic nanostructures that exhibit geometric asperities are likely to provide enhanced sensitivity compared to isotropic particles. Unfortunately, the optical sensitivities for nanostructures with complex shapes must be determined experimentally because current theoretical modeling and computer simulation methods for complex geometries are computationally intensive and time-consuming. Thus, a combinatorial experimental approach that allows the rapid and high-throughput optical characterization of many structures of different size and shapes is desirable to rapidly optimize the design of such nanobiosensors. As proof-of-principle of this high-throughput optimization approach, arrays of nanostructures with varying geometries with minimal dimensions of 60 nm were fabricated on glass substrates by electron beam lithography. Scattering spectra were collected with a grating spectrometer simultaneously from several nanostructure configurations on a customized Zeiss Axiovert 200 under darkfield illumination. The characterization of the geometric dependence of the optical properties of the gold nanostructures could be experimentally determined in single snapshot mode at the individual nanoparticle level using this set-up. Studies on the optical sensitivity of these nanostructures in response to perturbation of their local refractive index are currently in progress.

BI-MoP38 Sensitivity Enhanced Biosensor by Prussian Blue Modified Electrode*, I.J. Yi,* *J.H. Kim, C.J. Kang, Y.S. Kim,* Myongji University, Korea

We propose a sensitivity enhanced biosensor by Prussian blue (PB) modified indium tin oxide (ITO) electrode. A PB film plays a significant role of electron-transfer. Capillary electrophoresis (CE) and amperometric method were adapted to our work. Microchip was fabricated with polydimethylsiloxane (PDMS) to form microchannels and ITO patterned glass in inexpensive and simple method. The PB film was electrodeposited on the working electrode of various conditions to obtain stable PB film. Atomic force microscopy (AFM) was used to observe the changes of PB film surface. Calibrated PB film deposition voltage and time were obtained by AFM topography which shows PB surface characteristics. The optimized thickness of stable PB film was obtained when deposition voltage was about 0.1 V for 3 min. We detected various concentrations of neurotransmitters (dopamine and catechol) and hydrogen peroxide which is for detecting glucose respectively. It is observed that there was 20 times higher peak current for PB/ITO electrode than that for previously reported ECDs using bare-ITO electrode.@footnote 1@ Results are indicating rapid separation and detection of the analytes. The measured peaks of dopamine, catechol and hydrogen peroxide were proportional to their concentrations. When PB-modified electrode was used, the sensitivity was improved compared with bare-ITO electrode. It is believed that the PB film can be a viable candidate for a disposable and sensitive biosensor. @FootnoteText@ @footnote 1@Ju-Ho Kim, C. J. Kang, and Yong-Sang Kim, "A Development of a Microfabricated Disposable Microchip with a Capillary Electrophoresis and Integrated Three-Electrode Electrochemical Detection", Biosensors & Bioelectronics, vol.20, no.11, p.2314-2317, (2005).

BI-MoP39 Organosilane SAMs as a Platform to Tune the Immunosensor Performances*, R. De Palma,* IMEC vzw, Belgium*; S. Peeters,* KULeuven, Belgium*; K. Jans, K. Bonroy,* IMEC vzw, Belgium*; S. Cappelle,* Cytec Surface Specialities, Belgium*; G. Reekmans, W. Laureyn, G. Borghs, C. Van Hoof,* IMEC vzw, Belgium*; G. Maes,* KULeuven, Belgium

A central requirement in the modification of immunosensor interfaces with biological receptors is to tether the biomolecule of interest covalently and in a well-controlled geometry. A key issue in the design of these sensors involves the development of a sensitive, specific, reproducible and tunable biological interface. Self-assembly of silanes is commonly used as an effective surface modification tool in micro-array applications. However, most silanes used for micro-array are optimized towards DNA applications. Using quartz crystal microbalance (QCM-D), we have shown that the use of these silanes for immunosensing leads to inadequate characteristics, i.e. low sensitivity and specificity. Here we report on the enhanced immunosensing performances of novel preactivated silane SAMs. These preactivated functions allow for the direct coupling of receptors, thereby increasing the amount of immobilized antibodies. Using these preactivated silanes, the antibody immobilization was found to be reproducible, straightforward and controllable and the activity of the immobilized receptors was retained. Due to the molecular architecture of these silanes, the sensitivity, detection limit and specificity increased significantly. The degree of non-specific adsorption could be tuned by using appropriate blocking agents. Furthermore, a synthesis route was developed to create PEG-modified preactivated silanes. Deposition of these silanes in mixed silane SAMs allows for the creation of tunable immunosensing platforms. The silane-based interfaces were also compared to the well-known system of mixed thiol SAMs. The molecular architecture of all deposited silane SAMs was studied using contact angle, XPS, cyclic voltammetry, AFM and RAIRS. A strong correlation was observed between the layer characteristics and their immunosensing properties. Our approach based on preactivated silane SAMs guarantees a tunable and versatile platform for surface engineering in biosensing and micro-arrays.

BI-MoP40 In Situ Optical Characterization of an Electrodeposited Biopolymer Film*, **S.B. Beatty**, J.J. Park, E.C. Dreyer, G.W. Rubloff,* University of Maryland

We have previously demonstrated spatially selective, voltage-programmable deposition of the polysaccharide chitosan onto patterned electrodes in low pH solution. We have previously shown that chitosan, an amine rich biopolymer, serves as a useful platform for coupling and conjugation of biomolecules as well as a platform for bioassays and enzymatic catalysis. We have developed an optical reflectivity technique for real-time, in-situ monitoring of the electrodeposition process, demonstrated in a combinatorial deposition cell in concert with real-time electrical (current, voltage) and environmental (pH, temperature) measurements. A beam splitter separates a HeNe laser beam into a reference beam and an incident beam onto the electrodeposition surface in solution. A chopper separates the reflected beam from the surface and the reference beam in time, while both impinge on the same reversed bias Si photodetector. The resulting signal is analyzed to extract the ratio of reflected to reference beam intensities, averaged over an appropriate portion of the chopper period, providing a real-time measure of the reflectivity. Chitosan deposition on the Au electrode decreases reflectivity by about 16% for 1 micron chitosan thickness, with noise levels suggesting a thickness sensitivity of 60nm. Film growth rates vary with current density as seen in reflectivity and confirmed by ex-situ post-process characterization using profilometry and AFM. The reflectivity indicates three stages in chitosan film growth. We plan to extend the technique for use in a confocal optical microscope so that dynamic behavior at active bioreaction sites in a microfluidic network can be monitored.

BI-MoP41 Nano-mechanical and Chemical Mapping Showing Remineralization of Incipient Carious Lesions in Human Dental Enamel*, **M.E. Dickinson**,* Hysitron, Inc.*; A.B. Mann,* Rutgers, The State University of New Jersey

Human dental enamel consists of hydroxyapatite crystals arranged in a complex nano-scale prism structure. This architecture can be altered by chemical variations originating from dietary components and their interactions within the oral cavity. Temporary localized fluctuations of pH on the enamel surface create a flux of minerals into and out of the enamel which normally remains at an overall equilibrium. However, at continually low pH a net loss of mineral from the enamel results, causing the formation of an incipient carious lesion. The lesion - a stage prior to caries formation, is reversible and with specialized care such as remineralization treatments, can become arrested. Many commercial remineralization treatments use topical solutions containing fluoride and calcium phosphates to aid in caries prevention. However, the effect of these treatments at different stages of lesion progression is poorly understood. This investigation uses nanoindentation and TOF-SIMS to create high resolution mechanical and chemical maps of the lesion cross-section at different stages of demineralization. These lesions were analyzed before and after treatment with a commercial remineralization solution to study the effectiveness of remineralization at different stages of lesion progression. The results showed that the treatment acted to remineralize the lesion body for all lesions. However, the most demineralized lesions which had a different structure (no detectable surface zone), resulted in a different, possibly fluoroapatite based material being deposited at the base of the lesion with mechanical properties much higher than that of enamel. The chemical data correlated with the mechanical data to relate the structural integrity of the enamel with the change in hardness and reduced elastic modulus. Visualizing this dependence of lesion structure for efficient remineralization allows further understanding into the effectiveness of commercial dental treatments.

DNA Topical Conference
Room Exhibit Hall C&D - Session DN-MoP

DNA Poster Session

DN-MoP1 DPN-fabricated Au Microarrays on Si(111) Surfaces for the Site-Selective Immobilization of DNA*, **I. Kaoru**, I. Takahiro, L. SunHyung, S. Nagahiro, T. Osamu,* Nagoya University, Japan

Scanning probe-based lithography allow us to fabricate sub-100 nm structures on surfaces. Dip-pen nanolithography (DPN) is a new promising scanning probe-based tool for fabricating sub-100 nm to many micrometer structures on surfaces, since it is a method for directly depositing metal from an ink-coated atomic force microscope (AFM) tip onto a substrate with a high spatial resolution. In addition, DPN can draw the arbitrary metal patterns on the desired positions without complicated treatments. Thus, it is appropriate to apply DPN to the fabrication of biosensors on Si semiconductor. In order to develop such sensor devices, it is necessary to establish not only a fabrication technique of metal pattern but also an immobilization method of biomolecules on the pattern. In this study, we aim to fabricate Au microarray by DPN and immobilize DNA on the microarray. n-type Si(111) wafer (4-6 Î© cm) were used as substrate. Firstly, the substrate surface was cleaned by a UV/ozone cleaning method. Next, the Si substrate was terminated with hydrogen by wet etching of HF for 15 min. Au microarrays were then directly drawn on hydrogen-terminated silicon substrate using an AFM through DPN. DNA was selectively deposited on the Au microarrays through Au-S bonds. The surface constructed was traced by an AFM and fluorescence-labeled spheres.

DN-MoP3 PNA Microarray Development and DNA Diagnosis with TOF-SIMS*, **H.F. Arlinghaus**, S. Hellweg,* Westfälische Wilhelms-Universität Münster, Germany*; T. Grehl, E. Niehuis,* ION-TOF GmbH, Germany*; A. Jakob, J. Hoheisel,* Deutsches Krebsforschungszentrum Heidelberg, Germany

TOF-SIMS was used for the detailed examination of the immobilization process of PNA and its hybridization capability to unlabeled complementary DNA fragments. PNA sequences were immobilized onto SiO@sub 2@ and Au surfaces using different linking mechanisms. Unlabeled single-stranded DNA was hybridized to these biosensor chips containing both complementary and non-complementary immobilized PNA sequences. The hybridization of complementary DNA could readily be identified by detecting phosphate-containing molecules from the DNA backbone such as PO@sub 3@@super -@. The achieved discrimination between complementary and non-complementary sequences was very good. Further investigations were conducted regarding the influence of length and type of spacer molecules on the hybridization efficiency. The spacer molecule defines the distance between the PNA molecule and the biosensor chip surface. It was observed that a greater spacer length leads to higher hybridization efficiency. Using different primary ions, secondary ion yield behavior and fragmentation patterns were studied. This included monoatomic ions (Ar@super +@, Xe@super +@, Au@super +@, Bi@super +@) as well as polyatomic and cluster ions (SF@sub 5@@super +@, Au@sub x@@super +@, Bi@sub x@@super +@). It was found that using polyatomic and cluster primary ions resulted in a significantly increased yield of DNA-correlated fragments, resulting in higher signal intensities and better signal-to-noise ratios. It can be concluded that TOF-SIMS is undoubtedly a highly useful technique for identifying unlabeled hybridized DNA on PNA biosensor chips. It may provide a rapid method for DNA diagnostics and is suitable for studying the complexity of the immobilization and hybridization processes.

DN-MoP4 In-situ Observation of DNA Immobilization and Hybridization on Si by Surface Infrared Spectroscopy*, **K. Ishibashi**, R. Yamaguchi, K. Miyamoto, Y. Kimura, M. Niwano,* Tohoku University, Japan

We have previously proposed a label-free DNA sensing method by the use of infrared absorption spectroscopy (IRAS) in the multiple internal reflection (MIR) geometry, and demonstrated that hybridization of DNA oligomers dissolved in a buffer solution exhibits specific infrared spectral changes.@footnote 1@ In order to apply our method to DNA chips, we need to immobilize single-stranded DNA (ssDNA) oligomers, which are called "probe DNA", on a Si substrate surface. Furthermore, we need to control on the molecular scale the DNA immobilization process on Si to accomplish a precise analysis of DNA on a chip surface. In this study, we have used MIR-IRAS to in-situ investigate the chemical state of a Si substrate surface at each stage of DNA immobilization process, and to in-situ detect hybridization of immobilized DNA oligomers. MIR-IRAS has quite high surface-sensitivity because of the large number of internal reflections, and enables us to in situ monitor the chemical state of a Si surface in aqueous solution. Thiol-modified, 20-based ssDNA oligomers were immobilized on a Si surface that was modified with 3-aminopropyltrimethoxysilane (APTMS) andã??sulfosuccinimidyl 4-(N-maleimidomethyl)cyclohexane-1-carboxylate (SSMCC). On the basis of IRAS data, we confirmed that ssDNA oligomers were immobilized on a Si surface through covalent bonds. The immobilized ssDNA oligomers were subsequently hybridized with complementary ssDNA oligomers in a sodium chloride solution. We observed specific IR spectral structures at the region of 1600 to 1750 cm-1 that are due to DNA hybridization. The present results indicate that MIR-IRAS is a promising technique used for a label-free DNA sensing device. @FootnoteText@ @footnote 1@ Miyamoto K, Ishibashi K, Hiroi K, Kimura Y, Ishii H, Niwano M, Appli Phys. Lett. 86 (2005) 053902-1.

DN-MoP5 Organophosphonate Monolayers as Functionalisation for Silicon Based Biosensing Devices*, **E. Pringsheim,*** Walter Schottky Institute, Technical University of Munich, Germany*; M. Dubey,* Princeton University*; K. Buchholz,* Walter Schottky Institute, Technical University of Munich, Germany*; K. Arinaga,* Fujitsu Laboratories Ltd., Japan*; M.D. Carolus, J. Schwartz,* Princeton University*; M. Tornow, G. Abstreiter,* Walter Schottky Institute, Technical University of Munich, Germany

Planar semiconductor sensing devices based on silicon substrates have immense potential for applications such as label-free, fast, and time resolved detection of biomolecule binding events due to their great sensitivity to surface potential changes via the field effect.@footnote 1@ Phosphonate films are particularly suitable as functionalisation for such devices since they are easy-to-apply and provide for stable silicon surface derivatisation due to dense, self-assembled monolayers (SAMs) that bond strongly to the native silicon oxide. These SAMs can be modified with tailored, substituted end groups.@footnote 2@ We have investigated the covalent linkage of thiol-terminated Cy3 labelled DNA-oligonucleotides to functionalized alkylphosphonate layers assembled on silicondioxide by variation of the immobilisation parameters, including concentration of DNA, concentration of sodium chloride and immobilisation time. Hybridization with complementary strands and the coupling of the model protein avidin to biotinylated DNA is detected optically. Concepts for biofunctionalisation of field effect sensor devices via phosphonic acid monolayers will be discussed. @FootnoteText@ @footnote 1@ M. G. Nikolaides et al., ChemPhysChem, vol. 4, 1104-1106 (2003)@footnote 2@ K. S. Midwood et al., Langmuir, vol. 20, 5501-5505 (2004).

DN-MoP6 SPR Imaging Detection of DNA Hybridization/Adsorption with Exonuclease III Enzymatic Reaction*, **H.J. Lee**, R.M. Corn,* University of California, Irvine

DNA microarrays are emerging as a powerful tool for gene analysis, viral identification, medical diagnostics and many other biological applications. The next generation of DNA microarrays for biosensing will utilize both surface bioaffinity interactions and subsequent surface enzyme reactions on the adsorbed species in order to greatly enhance the specificity and sensitivity of the biosensor. For instance, we have recently demonstrated a novel approach that utilizes the enzyme RNase H in conjunction with RNA microarrays for the direct detection of DNA at femtomolar concentrations with surface plasmon resonance (SPR) imaging. In this presentation, we demonstrate the use of enzyme Exonuclease III, which specifically digests duplex DNA, in conjunction with DNA microarrays for the amplified SPR imaging detection of single stranded target DNA. Kinetic measurements of the surface Exo III reaction as a function of temperature and enzyme concentration were performed using a combination of SPR imaging and SPR fluorescence. Greater insight into the surface enzyme reaction was achieved through analysis using a newly developed kinetics model that couples the contributions of both enzyme adsorption and surface enzyme reaction kinetics.

DN-MoP7 Secondary Structure Effects on DNA Hybridization in Solution and on Surfaces*, **Y. Gao**, L.K. Wolf, R.M. Georgiadis,* Boston University

The hybridization process in which a DNA probe strand binds to its complementary target, is the basis of many biological assays. For short oligonucleotides in solution, secondary structure effects on duplex formation kinetics are well known. In contrast, these effects are less understood for surface interactions and some recent work concludes that hybridization at surfaces is not affected by secondary structure. In this work, the effect of secondary structure on DNA hybridization is studied systematically by UV-vis and surface plasmon resonance (SPR) in solution and on the surface, respectively. Hybridization kinetics were measured for thermodynamically equivalent sequences with varying degrees of single-stranded secondary structure. Our results indicate that duplex hybridization in solution is always one or two orders of magnitude faster than hybridization on the surface, depending on the extent of secondary structure. In addition, we find a direct relationship between the number of base pairs involved in secondary structure and the observed association kinetic rate constants in both environments. On the surface, secondary structure also affects hybridization efficiency. DNA sequences lacking secondary structure achieve equivalent hybridization efficiencies regardless of bulk solution ionic strength. However, as ionic strength is reduced, sequences with secondary structure achieve drastically reduced efficiencies. The binding equilibrium is affected because of the competition between duplex formation and single-strand unfolding.

DN-MoP8 Hybridization of Platinum Drug Adducts*, **L. Postelnicu**, R.M. Georgiadis,* Boston University

Hybridization of platinum drug adducts DNA is generally considered the major pharmacological target of platinum drugs. As such it is of considerable interest to understand the patterns of DNA perturbation. The new antitumor trinuclear platinum compound [{trans-PtCl(NH3)2}2Âµ-trans-Pt(NH3)2{H2N(CH2)6NH2}2]4+ (designated as BBR3464) is a highly charged compound, non-cross resistant with cisplatin in many human tumor xenografts. The enhanced binding of BBR3464 to single stranded DNA and RNA substrates suggests additional pathways for disrupting cellular function different from the traditional cisplatin. Single strand DNA is present during replication, transcription, recombination and repair. Here, we investigate how DNA hybridization is perturbed by the presence of a single platinum drug bound to one of the DNA strands, using BBR3464 and cisplatin DNA adducts. We use surface plasmon resonance (SPR) spectroscopy to monitor both free DNA and DNA adducts hybridization to a surface immobilized complementary DNA strand. We characterize and compare the hybridization rate constants of cisplatin and BBR3464 DNA adducts at different ionic strength. BBR3464 is a large and highly charge structure compared to cisplatin. The results suggest that the charge of the drug is less important in the hybridization event, and the steric hindrances due to different structures may be more important for hybridization efficiency and kinetics.

DN-MoP9 Characterization of dNTP and ssDNA Attached to Diazonium-modified Surfaces*, **D. Barbash**, J.E. Fulghum, G.P. Lopez,* University of New Mexico

The immobilization of ssDNA to various modified substrates is utilized in wide-ranging applications including DNA microarray technology and molecular wires. Surface and near-surface characterization techniques such as x-ray photoelectron spectroscopy (XPS) and ATR-FTIR have been demonstrated to be useful in the characterization of attached nucleotides (dNTPs). In this work we use dNTP-based systems as a model for more complex systems. The dNTPs can be uniquely identified using either XPS or ATR-FTIR. Orientation of the attached dNTPs was investigated by ARXPS and found to be consistent with the expected attachment chemistry. Principal component analysis (PCA) on the ARXPS data was utilized to both enhance identification of chemical species and to confirm orientation. ARXPS, ATR-FTIR and multivariate analysis methods have been applied to the study of ssDNA attachment to diazotized surfaces. We will discuss the use of these methods, in combination with data on dNTP attachment, for identifying the orientation of attached ssDNA.

DN-MoP10 DNA Mobility through 2-D Entropic Well Lattices with Nanoscale Constrictions*, **E.A. Strychalski**, H.G. Craighead,* Cornell University

We are examining the interactions of double stranded DNA with novel micro- and nanofluidic geometries in order to gain an understanding of DNA mobilities through these fluidic structures. In particular, we are constructing various two dimensional arrays of wells through which double stranded DNA are electrophoretically driven. Each well serves as an entropic trap, affecting DNA mobility in a way that inhibits the migration of smaller strands relative to longer strands. While this behavior was first described by Han and Craighead in one dimensional entropic arrays,@footnote 1@ our work seeks to establish the effects of extending the entropic array to two dimensions. Our well lattices typically extend 500 microns down the length of a 500 micron wide channel. These channels are at most 50 nanometers deep between micron deep circular wells with well spacings from 5 to 20 microns. The two dimensional structure of our entropic arrays allow the investigation of varied well diameter, lattice structure, lattice constant, and lattice offset angle relative to the direction of the applied electric field. We report on the effectiveness of various entropic well lattices, embedded in nanoscale fluidic channels, to yield DNA separation. @FootnoteText@ @footnote 1@ J. Han, H.G. Craighead, J. Vac. Sci. Technol. A. 17, 2142 (1999).

MEMS and NEMS
Room Exhibit Hall C&D - Session MN-MoP
General Aspects of MEMS and NEMS Poster Session

MN-MoP1 AFM Studies of Conditioner Thickness Distribution and Binding Interactions on Hair Surface*, **B. Bhushan**, N. Chen,* The Ohio State University

How common hair care products, such as conditioner, deposit onto and change hair properties are of interest in beauty care science, since these properties are closely tied to product performance. The binding interaction between conditioner and hair surface is one of the important factors in determining the conditioner thickness distribution, and consequently the proper functions of conditioner. In this study, AFM is used to obtain the local conditioner thickness distribution, adhesive forces and effective Youngâ?Ts modulus mapping of various hair surfaces. The conditioner thickness is extracted by measuring the forces on the AFM tip as it approaches, contacts, and pushes through the conditioner layer. The effective Young's moduli of various hair surfaces are calculated from the force distance curves using Hertz analysis. The binding interactions of different silicones on the hair surface, as well as their effect on the effective Young's modulus of the hair are also discussed.

MN-MoP2 Plasma Enhanced Chemical Vapor Deposition of Low Stress Silicon Nitride Using Diethylsilane as Precursor*, **L.M. Fischer**, S. McColman, B. Szeto, K. Westra, S. Evoy,* University of Alberta, Canada

The stable surface and high stiffness-to-density ratio of silicon nitride offer interesting advantages over regular silicon for the production of high-frequency and high-quality nanoelectromechanical (NEMS) resonators. Such machining however requires a mechanical material possessing very low residual stress. Silicon-rich low-stress silicon nitride is typically produced using silane/nitrogen or silane/ammonia as precursors. Silane is however highly flammable and thus poses significant safety hazard. In addition, typical low-stress films produced by these methods may still contain residual stress levels exceeding 100 MPa. We here report the PECVD of silicon nitride using the relatively safer diethylsilane (DES) as precursor. We also report the control and reduction of residual stress in the films through post-deposition anneal. Compressive residual stress in the as-deposited material ranged from 555 MPa to 1GPa as the NH3:DES ratio varied from 1:1 to 16:1, while nitrogen content increased and carbon content decreased over the same range. This correlation is related to the increased formation of N-H radicals within the films. Compressive residual stress also increased from 558 MPa to 849 MPa as the deposition temperature was varied from 240 C to 315 C. Such temperature dependence is in turn attributed to an increased densification of the deposited films. A post-deposition anneal in inert nitrogen at temperatures of 500 to 600 C however relieves the stress and enables its control from the compressive to the tensile range. Tensile stresses as low as 50 MPa have been achieved. While hydrogen desorption is believed to be responsible for this change, XPS analysis also provided evidence of the formation C-N bonds in the annealed films. We will report a complete analysis of the formation, stochiometry, and stress relief in these films. We will also present the machining and characterization of NEMS resonators in this low-stress material.

MN-MoP3 DNA Detection System using a Microcantilever*, **K.-A. Yoo**,* Myongji University, Korea*; K.-H. Na,* Lite-on Technology Corp. Korea*; S.-R. Joung, C.J. Kang, Y.S. Kim,* Myongji University, Korea

We propose a novel detection system for analysis various biotinylated DNAs effectively with a microcantilever. The microcantilevers were fabricated employing surface micromachining technique that has attractive advantages in terms of cost efficiency, simplicity and ability of fabricating in array. The fluid cell system for injection of bio-molecular solution is fabricated using a polydimethylsiloxane (PDMS) and a fused silica glass. The microcantilever is deflected with respect to the difference of the surface stress caused by the formation of self-assembled bio-molecules on the gold coated side of the microcantilever. It can detect various biotinylated DNAs according to the specific interactions between the streptavidin and individual DNA sequencing of biotinylated DNA. We confirm that the deflections of bending-up or bending-down of individual microcantilevers are occurred by the bio-molecule adsorption. The microcantilever detected protein A and DNA due to the specific interaction between protein A and DNA. The principle of the interaction is a self-assembly between the bio-molecules. The microcantilever can be widely used to detect various bio-molecules including specific DNA and can be utilized as a bio-sensor.

MN-MoP5 Novel Fabrication Method of a Master Structure for Replicating an Optical Device Including Vertically Curved Structures*, **M.W. Lee**, K.J. Lim, C.H. Choi, S.B. Jo, S.G. Lee,* Inha University, Korea*; S.G. Park,* Inha University, Korea, Korea, Republic of*; B.H. O,* Inha University, Korea

Replication process is a good way to fabricate a passive optical device. Silicon based fabrication technology provides an efficient way to fabricate a master structure with optically smooth surface roughness. As silicon based technologies are often 2 dimensional processes, replication process requires a sophisticate fabrication steps for a master structure. For that reason, a vertically curved structure which is essential for a passive optical device is hard to fabricate. Some special processes, such as x-ray lithography, laser ablation, and gray-scale mask can overcome the conventional 2-dimensional fabrication process. But the processes need additional process steps, machines and masks. This study demonstrates easy way for fabricating a silicon master structure with vertically curved mirrors. This fabrication method is roughly divided into two steps. At the first step, a silicon wafer was deeply etched by using ICP system, to form the waveguide structures in the master structure. The vertically curved mirror structures at the each ends of the waveguides, are formed by using photoresist reflow process of the second step. After the master fabrication, the master shape was transferred to a PDMS mold. Replication process was carried by using UV curable polymers, and successful vertical redirection of lights at the curved structure was observed with a CCD device. The surface roughness of the replicated structure was also measured, and an optically smooth surface roughness was observed. Detailed fabrication steps and the fabricated device characteristics will be discussed.

MN-MoP6 CO Gas Sensor based on a Doped ZnO Film with a Microhotplate/Floating-Gate MIS Structure*, **W. Calleja-Arriaga**,* Inaoe Mexico, MEXICO*; J. De la Hidalga-Wade,* Inaoe Mexico*; A. Heredia-Jimenez,* Upaep Puebla-Mexico*; G. Rosas-Guevara, I. Juarez-Ramirez, C. Zuñiga-Islas, N. Carlos-Ramirez, P. Alarcon-Peña, L. Tecuapetla-Quechol, M. Escobar-Aguilar, J. Silva,* Inaoe Mexico*; J.L. Gonzalez-Vidal,* Citis-Uaeh Mexico*; M.A. Reyes-Barranca, M.L. Olvera, A. Maldonado,* Cinvestav Mexico

Doped and undoped zinc oxide (ZnO) single thin films, used as the active element in a gas microsensor, is presented in this work. The gas sensor arrangement is based on a double polysilicon micro-hotplate (MHP) and a polysilicon floating gate MIS transistor (FG-MIS). The ZnO films were doped with 6% of either copper, chromium, or gallium. The ZnO film, with an active area of 80x80 microns, was deposited onto a polysilicon plate that forms the gate of the MIS transistor. This sensing section is heated by a U-shaped polysilicon stripe, which is located beneath the polysilicon plate and electrically isolated from it by nitride/oxide films. The microhotplate is thermally isolated using a deep cavity micromachined in the silicon substrate, and mechanically supported by four polysilicon arms. The sensing film induces a charge in the floating-gate in such a way that the channel conductance is modulated. The sensor structure was characterized by detecting carbon monoxide (CO) at 300 ÂºC. Finally, a complete procedure of fabrication of this sensor structure will be presented at the conference.

Plasma Science and Technology
Room Exhibit Hall C&D - Session PS-MoP
Plasma Science and Technology Poster Session

PS-MoP1 Minimum Area Required for Poly Etch Endpoint Detection*, **R.L. Hill**,* National Semiconductor

There have been somewhat arbitrary design rules implemented over the years dealing with how much open (non-resist covered) area is required on a product layout at a given layer to ensure robust endpoint detection. Design rules have been used at the typical layers that employ endpoint detection, e.g. poly, isolation, metal, capacitor. A systematic study of the poly layer endpoint detection is discussed in this report. A photolithographic method is introduced to measure the open area required for endpoint detection. Two etchers are studied: Lam 4400 poly etcher and a higher plasma density Lam TCP 9400SE. The endpoint signal versus percent open area and etch rate versus percent open area are presented. The minimum reticle open area required for the Lam 4400 endpoint detection was determined to be 25% and for the Lam 9400 it was

30%. Neither etcher showed an etch rate dependence on the percent open area.

PS-MoP2 Optical Second Harmonic Generation during Ar@sup +@ Etching of Silicon*, **P.M. Gevers**, A.A.E. Stevens, J.J.H. Gielis, H.C.W. Beijerinck, M.C.M. Van De Sanden,* Eindhoven University of Technology, The Netherlands*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands

Plasma etching of crystalline silicon can create a damaged layer in the top region of the silicon due to ion bombardment. Defects like strained and dangling silicon bonds are expected to be abundant in this region. The surface and interface sensitive nonlinear optical technique of second harmonic generation (SHG) is known to probe these defects in crystalline silicon and is therefore applied to study the plasma etching process. To circumvent the complexity of the plasma, the experiments are performed in a UHV multiple-beam setup, containing an ion source producing Ar@sup +@ ions with energies ranging from 20 eV to 2.5 keV. The data presented here will discuss the SH-signal in the photon energy range of 2.70-3.44 eV probing the strain-induced resonance. The silicon SH-signal exhibits an enormous increase when subjected to Ar@sup +@ ions. Careful analysis has localized the origin of the signal to both the surface of the silicon and the interface between the damaged and crystalline silicon. Future application of this diagnostic in the ion induced etching process promises to aid in the understanding of the etching process and might supply the possibility of monitoring the defects induced during processing.

PS-MoP3 The Study of Atomic Layer Etching Mechanism for Si with Various Substrate Orientations*, **S.D. Park**, C.K. Oh, M.S. Kim, G.Y. Yeom,* Sungkyunkwan University, Korea

Atomic layer etching (ALET) can be an indispensable method in the fabrication of future devices such as nano-scale devices, quantum devices etc., because current etch technology utilizing reactive ion etching dose not have precise etch rate controllability and tends to damage the surface of the devices physically and electrically due to the use of energetic reactive ions to achieve vertical etch profiles. Generally, ALET of Si is composed of a cyclic process consisted of 4 steps; (1) adsorption of Cl@sub2@ on the Si surface, (2) evacuation, (3) Ar@super+@ ion beam irradiation to the substrate surface for desorption, (4) evacuation of the etch products. But, if Ar@super+@ ion beam is used for the desorption, the etched substrate can be charge damaged due to the charged particles such as positive ions and photons generated in the plasma. In this study, the ALET of Si was carried out for the first time using an Ar neutral beam instead of the Ar@super+@ ion beam to avoid charge-related damage during the desorption of halide and its ALET characteristics of Si by Cl@sub2@ were investigated. Especially, the ALET of Si having different orientations were investigated to understand the silicon etch rate per cycle.

PS-MoP4 The Effect of Oxide Thickness on Photoemission and Photoconduction Currents during VUV Irradiation*, **J.L. Lauer**, J.L. Shohet, G.S. Upadhyaya,* University of Wisconsin-Madison

Vacuum ultraviolet (VUV) radiation with photons in the energy range of 5 to 20 eV produced by high-density plasmas in plasma-processing systems can cause degradation to devices by changing the optical, mechanical, chemical and electrical properties of dielectrics. This is particularly important for thin films used in intermetal dielectric layers, because VUV is absorbed by the dielectric layer. Radiation charging of Si wafers coated with SiO@sub 2@ of different thicknesses in the range of 3000Å to 200Å was made by exposing them to synchrotron VUV radiation with photon fluxes in the range of 10@super 10@ -10@super 11@ photons/sec cm@super -2@ and photon energies of 7, 10, and 13 eV. The photoemission current and the current drawn by the substrate were monitored during each exposure. The tunneling and/or photoconduction current drawn through the oxide layer can be found by subtracting the photoemission current from the current drawn by the substrate. The total charge induced on the dielectric during VUV exposure consists of charge due to photoemission and electron-hole-pair creation, the net amount of which can be measured with a Kelvin Probe. The tunneling current (electrons injected from the silicon substrate into the oxide layer) causes a decrease in the charge produced by photoemission and electron-hole-pair creation. For most dielectrics, the threshold photon energy for photoemission is higher than that for electron-hole-pair production. The photoemission current can be minimized while the tunneling/photoconduction current increases, if the photon energies are below the threshold energy for photoemission but larger then the bandgap energy. VUV-exposed SiO@sub 2@ of various thicknesses shows the photon penetration depth as a function of energy and allows a quantitative description of the mechanisms that are involved in the photoconduction/tunneling processes taking place. @FootnoteText@ Work supported by NSF under Grants DMR-0306582.and DMR-0084402. .

PS-MoP5 Reduction of Gate Oxide Plasma Induced Damage via Silicon Nitride Backside Film*, **H. McCulloh**, C. Bossie, P. Allard, J. Garmon, C. Printy,* National Semiconductor

Plasma charging damage continues to be an issue in advanced semiconductor processing. In this work, the effect of residual films on the backside of the wafer on plasma damage induced at interconnect layers is investigated. Our experimental results show that intermetal dielectrics formed using fluorinated high density plasma (FHDP) are particularly prone to causing plasma induced damage (PID). The current work shows that residual material on the backside of the wafer has a strong impact on this damage. It is proposed that the presence of a conductive or semi-conductive backside film contributes to PID via electrical coupling through the electrostatic chuck (ESC) during the FHDP deposition process. Our results show that the presence of a uniform silicon nitride film on the back of the wafer dramatically reduces gate oxide damage caused by PID. Different backside film integration schemes were studied. PID was evaluated using metal antenna style test structures, with FHDP being deposited directly on the antenna.

PS-MoP7 Study of the Plasma-Induced Damage by Inductively Coupled Plasma in Pb(Zr,Ti)O@sub 3@ for FeRAM(Ferroelectric Random Acess Memory) Devices*, **H.Y. Ko**, K.R. Byun, Y.J. Jung, D.H. Im, D.C. Yoo, S.H. Joo, J.H. Ham, S.H. Park, H.S. Kim, K.K. Chi, C.J. Kang, H.K. Cho, U.I. Jung, J.T. Moon,* Samsung Electronics, South Korea

FeRAM is a non-volatile memory device based on the remnant polarization of ferroelectric film such as Pb(Zr,Ti)O@sub 3@ (PZT). The electrical properties of PZT films have proven to be excellent enough to apply to high-density FeRAM with 1T1C cell structure, in terms of the high remnant polarization and low crystallization temperature. However, it is known that high-density integration gives rise to several problems such as plasma-induced damage of PZT surface and surface composition change, which degrade FeRAM capacitor performances during the patterning of capacitor module. In this article, we carried out the investigations of the plasma-induced etching damage for the PZT thin films etched with the various gases chemistries (O2, Ar, BCl@sub 3@, Cl@sub 2@, CF@sub 4@, and mixture gases) on the microstructural and electrical properties. We analyzed the effect of individual and mixture gases on the near surface chemistry of the PZT thin films by XPS(X-ray Photoelectron Spectroscopy). We also used TEM(Transmission Electron Microscopy) and AFM(Atomic Force Microscope) for the structural and compositional change and roughness in the film through patterning of the real FeRAM devices. Finally, we evaluated the electrical properties (2Pr, fatigue, leakage current, retention) of the plasma-exposed PZT films through patterning of the real FeRAM devices.

PS-MoP8 Effective Stripping of Heavily Implanted Photoresist by Insitu-Bake Process*, S.-K. Yang,* Inha University, Korea*; J. Yang,* PSK Inc.*; **S.G. Park**,* Inha University, Korea, Korea, Republic of

Popping of heavily implanted photoresist during plasma stripping, which is the main source of particulate contamination, occurs during the conventional stripping process using oxygen radicals at the temperature range of 250°C or higher. We introduce in-situ bake process (ISBP) prior to oxygen plasma stripping which does not suffer from low ashing rate or substrate damage. It is found that baking wafers at 250°C in the atmospheric pressure before evacuating the process chamber accelerates outgassing from bulk of photoresist without popping. Since heat transfer from heating wafer stage to wafer is better in air than that in vacuum, the stripping rate is also increased 50% because time to reach the process temperature is reduced. In this paper, we show the evidence of no-popping during bake-in-air step and the surface modification by bake-in-air by XPS analysis of carbon bonding. XPS data shows that baking in vacuum enhances more amorphous carbons in the photoresist surface than baking in air.

PS-MoP9 Plasma Etching of High-k and Metal Gate Materials in High-Density Chlorine-Containing Plasmas*, **K. Nakamura**, T. Kitagawa, K. Osari, K. Takahashi, K. Ono,* Kyoto University, Japan

As ultra large scale integrated circuit dimensions continue to be scaled down, high dielectric constant (high-k) materials such as HfO@sub 2@, ZrO@sub 2@, Al@sub 2@O@sub 3@, etc. are being required as gate dielectric to maintain the gate capacitance in smaller size. Moreover, for a gate stack with high-k dielectrics, gate electrodes of conventional polycrystalline silicon (poly-Si) tend to cause some problems of the depletion layer present in doped poly-Si gate materials, thus being replaced by metal electrodes such as Pt, Ru, TaN, TiN etc. For the fabrication of high-k gate stacks, an understanding the etching characteristics and mechanisms is indispensable for high-k dielectrics as well as metal electrodes. However, only a few studies have recently been concerned with their etching for the application to high-k gate stacks. In this study, we have investigated the etching of high-k materials of HfO@sub 2@ and metal electrode materials of Pt and TaN using high-density chlorine-containing plasmas excited by electron cyclotron resonance. The etching of HfO@sub 2@ etching was performed in BCl@sub 3@ plasmas at around 10 mTorr without rf biasing, giving a high etch selectivity (>>1) over Si and SiO@sub 2@ was obtained. At lower pressures, some deposition was found to occur on all material surfaces. The etching of Pt was performed in Ar/O@sub 2@ plasmas with high rf biasing, where highly selective Pt etching was achieved over HfO@sub 2@, Si, and SiO@sub 2@ by adding O@sub 2@ to Ar. Moreover, the etching of TaN was performed in Ar/Cl@sub 2@ plasmas, where high etch rates and high etch selectivity of TaN over HfO@sub 2@, Si and SiO@sub 2@ were obtained with low rf biasing. The etched profiles of Pt and TaN were also investigated; the etched profile of Pt was positive tapered, while the profile of TaN was found to be almost anisotropic. This work was supported by NEDO/MIRAI project and by Taiyo Nippon Sanso Corp.

PS-MoP10 Effects of Non-Volatility of Etch Products on Surface Roughness during Etching of Advanced Gate Stack Materials*, **W.S. Hwang,*** National University of Singapore*; W.J. Yoo,* National University of Singapore, singapore

As device dimensions continue to shrink, it becomes very crucial to understand evolution of surface roughness of device structures during etching. Until now, the mechanism on roughness evolution of Si surface from which volatile etch products are generated has been studied by various researchers. However, surface properties of new conducting materials such as TaN, TiN, HfN, and IrO@sub 2@ have rarely reported, although several reports on etching properties of advanced gate electrodes have been reported. In this work, we investigate the effects of the plasma parameters of ion energy (E), ion current density (J@sub i@) and ratio of ion flux over neutral flux (J@super +@ / J@sub n@) on the evolution of surface properties of these materials during etching. Etch rates of all samples are seen to obey the following empirical relation of ER(t)=C@sub 1@ E J@sub i@ (J@super +@/J@sub n@) (t) where ER is etch rate. The same approach was made to understand the evolution of surface roughness. It was found that surface roughness and etch rate are inversely related each other when volatile byproducts are formed, as shown in the following relation of @sigma@(t)=C@sub 2@ 1/E 1/J@sub i@ (J@sub n@ / J@super +@) t where @sigma@ is roughness value, in that surface roughness is proportional to pressure but inversely proportional to bias voltage. This relation implies that anisotropic profile can be attained without sacrificing the surface roughness. On the other hand, it is found that surface roughness and etch rate are proportional each other when non-volatile byproducts are formed, as expressed in the relation of @sigma@(t)=C@sub 3@ E J@sub i@ (J@super +@ / J@sub n@) t. That is, the formation of nonvolatile residues promotes surface roughening during ion induced chemical etching. In addition, results show that the average lateral distance between peak to peak increases with increasing surface roughness due to the redeposition and agglomeration of nonvolatile byproducts.

PS-MoP11 Highly Selective W/WN/Poly-Si Etching by using RLSA Microwave Plasma Source*, **T. Nishizuka**, K. Song Yun, K. Ishibashi, T. Nozawa,* Tokyo Electron, LTD., Japan*; T. Goto, T. Ohmi,* Tohoku Univ., Japan

W/WN/Poly-Si stack is used as a gate material of DRAM. For the etching of W/WN layer, high density plasma sources, such as ECR, ICP, etc., are usually applied with Cl@sub2@+O@sub 2@ gases.@footnote 1@ An important requirement of this etching is selectivity to Poly-Si. The selectivity can be improved by increasing oxygen fraction. However, actual selectivity used to be 1 or so because oversupply of oxygen causes deposition which is attributed to oxidized etching by-products, WO@sub 3@. In this study, we developed a RLSA (Radial Line Slot Antenna) microwave plasma source, and evaluated it on the W etching process. It can generate uniform surface-wave plasma with low electron temperature without magnets,@footnote 2,3@ and therefore it has compact chamber which reduces gas residence time. As for gas chemistry, N@sub 2@ addition was evaluated along with Cl@sub 2@+O@sub 2@ gases condition. As a result, we obtained high selectivity>5, W etch rate>100nm/min and straight W profile under the condition of fairly low stage temperature=60°C. We also found N@sub 2@ gas addition in high flow rate was effective to achieve both high selectivity and good profile. The role of nitrogen appeared to contribute to variety of radicals in the plasma rather than nitridation of Poly-Si and W surface. It probably controls the amount of reactive Cl and O radicals then reduces oxidization of by-products and Poly-Si etching rate. Furthermore, no charge-up damage has been observed on antenna MOS structure under any conditions. We believe that the high density plasma with low electron temperature and short residence time of gases lead to those performances. @FootnoteText@ @footnote 1@ T. Umezawa et.al., 1998 Dry Process Symposium, p49.@footnote 2@ H. Kokura et.al., 1999 Dry Process Symposium, p209.@footnote 3@ T. Ohmi, Semiconductor Manufacturing, Nov.2003, p110.

PS-MoP12 Extremely Thin Silicon Oxide Formation Using Pulse-Time-Modulated Oxygen Neutral Beam*, **C. Taguchi**, S. Fukuda, S. Noda, S. Samukawa,* Tohoku University, Japan

For next generation ULSI devices, high-k gate dielectric film is promising candidate since it provides both low gate-leakage and minimal electrical thickness in inversion. It is also important to form ultra-thin SiO@sub 2@ film between high-k film and Si substrate to avoid forming silicate. To minimize EOT of gate dielectric films, sub-1 nm fine thin SiO@sub 2@ film formation is indispensable. However, it is much difficult for conventional thermal-oxidation-processes to realize the requirement. To break through the problem, we proposed pulse-time-modulated neutral beam oxidation. In this new method, low energy (less than 10 eV) O@sub 2@ neutral beam radiation was modulated to the silicon substrate at the time constant of a few tens of µ seconds. That is, the oxidation process was modulated on the silicon surface. We first found that the SiO@sub 2@ thickness could be precisely controlled by changing the beam-on time in the pulse-time-modulated O@sub 2@ neutral beams without any radiation damages. It is speculated that the injected O@sub 2@ was diffused at a time constant of a few tens of µ seconds in the silicon. As a result, extremely thin SiO@sub 2@ film of less than 1 nm (minimum thickness:0.5 nm) could be formed on the silicon substrate by using the pulsed O@sub 2@ neutral beams. Our newly developed method is promising candidate to replace the thermal-oxidation-processes.

PS-MoP14 A Comparative Study on Dry Etching of TaN/HfO@sub 2@ Gate Stack Structure in Inductively Coupled Plasmas using Cl@sub 2@, BCl@sub 3@, and HBr Chemistries*, **M.H. Shin**, M.S. Park, N.-E. Lee,* Sungkyunkwan University, Korea*; J.Y. Kim,* Kookmin University, Korea, Rep. of Korea

Development of advanced high-k gate dielectrics and its integration into advanced nano-scale CMOS devices below 50-nm technology node has gained considerable attention recently because of the need for the replacement of ultrathin SiO@sub 2@ or nitrided SiO@sub 2@ gate dielectrics. For the integration of the high-k gate dielectric materials in the nano-scale CMOS devices, metal gate electrodes are expected to be used in the future. Currently, the metal gate electrode materials including TaN, TiN, HfN, WN, TaSiN and metal silicides are being widely studied for next generation devices with high-k gate dielectrics. Among many integration issues, selective etching of metal gate electrodes and the high-k gate dielectrics over the Si substrate is expected to be one of critical steps in the process integration of the front-end of the line (FEOL). In this work, as a model system for studying the etching characteristics of the metal gate electrode/high-k dielectric stack structures and etch rate selectivity of the metal gate electrode over the high-k dielectric layer, TaN/HfO@sub 2@ gate structure, was chosen. ICP etching characteristics of TaN(150nm)/HfO@sub 2@(80nm) gate stack structures on Si substrate were investigated by varying the process parameters such as etch gas mixing ratios (Cl@sub 2@/Ar/O@sub 2@, BCl@sub 3@/Ar/O@sub 2@, and HBr/Ar/O@sub 2@), the top electrode power, the DC self-bias voltage (V@sub dc@), and working pressure in an ICP etcher. To understand the role of etch gas chemistry in ICP etching, the relative change in the densities of ion radical and chemical binding states of etched TaN and HfO@sub 2@ surfaces were measured by optical spectroscopy (OES) and X-ray photoelectron spectroscopy (XPS), respectively. The results of the etch rate and etch selectivity of SiO@sub 2@ to HfO@sub 2@ measured as a function of the various process parameters will be discussed in detail in conjunction with the OES and XPS analysis data.

PS-MoP15 Etching of Titanium Nitride*, **D. Wu**, B. Ji, E.J. Karwacki,* Air Products and Chemicals, Inc.

Titanium nitride (TiN) has many emerging new applications within semiconductor industry. It is being employed as a diffusion barrier in contacts, vias, trenches, and interconnect stacks, as well as an electrode material. The film is typically deposited by way of a batch CVD technique within a quartz tube furnace at a temperature lower than 150ºC. A cleaning method that removes TiN deposits from the inner surfaces of the deposition chamber, but does not damage the furnace is urgently needed by the industry. In this paper we report on our efforts to develop an effective process for TiN deposition chamber cleaning. Using our lab reactor as a screening tool, a variety of reactive gases and process conditions has been screened. For example, we have tested a thermal process using NF3, Cl2, and 5%F2. In each case, a temperature of higher than 200ºC is needed to start the etching reaction. To reduce the required temperature, remote plasma is used together with the thermal process. The process using remote NF3 plasma etches TiN at a rate of 1000 nm/min with a TiN/SiO2 selectivity of 8 at 140ºC. Surface analysis is also conducted to understand the etching mechanism.

PS-MoP16 Etching of Narrow Porous SiOCH Trenches using a TiN Metallic Hard Mask*, M. Darnon,* CNRS LTM - France, France*; N. Posseme,* ST Microelectronics - France*; D. Eon,* UJF - France*; T. David,* CEA LETI - France*; T. Chevolleau,* CNRS LTM - France, France*; L. Vallier,* CNRS LTM - France*; O. Joubert,* CNRS LTM - France, France

In CMOS technology, most of the interlayer dielectric materials achieve low k values by introducing porosity in order to reduce the total resistance capacitance (RC) delay in the interconnect levels. Trench or via patterns are transferred into porous SiOCH (p-SiOCH) using a dual hard mask strategy. This approach minimizes the porous low k degradation induced during ash plasma exposure. Different hard masks (metallic such as TiN or TaN and inorganic such as SiO@sub 2@ or SiC) are currently under investigation to pattern 65 nm trenches targeted for the 45 nm node. This work is dedicated to the analysis of the impact of a metallic hard mask used to pattern narrow porous SiOCH trenches etched in fluorocarbon based plasmas. The stack investigated is composed of 600 nm p-SiOCH, 40 nm SiO@sub 2@, 45 nm TiN and 100 nm photoresist (PR). The 200 mm wafers are patterned using direct ebeam lithography to achieve aggressive trenches dimensions down to 50 nm. After TiN opening and resist removal, the SiO@sub 2@ and p-SiOCH layers are etched in two different industrial etching chambers: either an inductive (ICP) or a capacitive (MERIE) plasma source. Chemical topography analyses by X Ray Photoelectron Spectroscopy (XPS) and ion mass spectroscopy show that the condensation of low volatile Ti based etch by-products on the trench sidewalls can generate severe profile distortions. The profile distortion is strongly minimized and even suppressed by increasing the wafer temperature from 20°C up to 60°C. The TiN hard mask consumption during the dielectric etch process can be reduced by using highly polymerizing chemistries which contributes to the formation of a fluorocarbon overlayer on top of the mask. The patterning of very narrow trenches reveals that one of the main issues is the faceting of TiN hard mask, leading to unacceptable profile distortions. The impact of the plasma parameters on the profile distortion of narrow trenches will be presented and discussed.

PS-MoP17 A Stacked Mask Process (S-MAP) for Precise CD Control using 100 MHz CCP RIE*, H. Hayashi,* *J. Abe, A. Kojima, I. Sakai, T. Ohiwa,* Toshiba Corporation, Japan

The stacked mask process (S-MAP)@footnote 1@ has been developed to provide improved critical dimension (CD) control in deep UV lithography, where it is necessary to use thin photo resist (P.R.) susceptible to etch erosion. In S-MAP, the P.R. pattern is first transferred to a spin-on-glass (SOG) layer, then to spun-on carbon film. An oxygen-based chemistry has been widely used for organic film etching. However, it tends to cause a bowed profile due to excess oxygen radicals. Therefore, a nitrogen-based chemistry is often used, where a straight profile can be obtained because of the sidewall protection effect by nitrogen. But, when the nitrogen-based chemistry was applied to the etching of stacked film structure such as S-MAP, the SOG film peeled at the interface of SOG and carbon films during etching under some conditions. The mechanism of SOG peeling in nitrogen-based chemistry was examined by analyses of the SOG/carbon stacked film after etching, and it was found that nitrogen gas was trapped in the stacked film. On the other hand, the SOG surface exposed to the plasma was densified by ion irradiation. It is assumed that, as etching progressed, nitrogen molecules gradually accumulated in the stacked film until the nitrogen gas pressure in the film became high enough to cause SOG peeling. By using the 100 MHz capacitive coupled plasma (CCP) which can realize low pressure and low ion energy simultaneously, carbon film etching using nitrogen-less gas chemistry without bowing was realized, by suppression of oxygen radical density at low pressure. Furthermore, selectivity to SOG improved because of the low ion energy, and CD loss due to SOG erosion was reduced. In conclusion, S-MAP for the 55 nm pattern size with precise CD control was realized by using 100 MHz CCP RIE using nitrogen-less gas chemistry. @FootnoteText@ @footnote 1@J. Abe et al., Symp. Dry Process, (2001) 187.

PS-MoP18 Characterization Methodologies for Unsaturated 1,3-C4F6 Plasma used to Investigate Aspect Ratio Dependent Etch and Etch Characteristics with Comparison to Saturated C-C4F8*, T.L. Anglinmatumona,* San Jose State University*; C.T. Gabriel,* Advanced Micro Devices*; E. Allen,* San Jose State University

The scaling of device features below 65 nm may encounter severe challenges such as the mass transport of CF2 and CF polymer precursors to the bottom of the feature due the generation of large molecular-weight radicals in saturated chemistries. As aspect ratios continue to increase due to the shrinking of the via hole diameter, saturated chemistries such as octafluorocyclobutane (c-C@sub 4@F@sub 8@) will no longer provide the etch performance required for ULSI. Hexafluorobutadiene (1,3-C@sub 4@F@sub 6@) is being proposed as an alternative gas to c-C@sub 4@F@sub 8@ for via etching in an inductively coupled plasma system. Profile slope, etch selectivity, CD bias and etch rates were investigated as a function of cathode temperature, rf bias power and chamber pressure. Optimum process conditions were identified based on a statistical design of experiment. Hexafluorobutadiene at optimized process conditions improved the etch parameters overall by 2X in comparison to c-C@sub 4@F@sub 8@. Aspect ratio dependent etching (ARDE) was reduced due to 1,3-C@sub 4@F@sub 6@ unsaturated bond configuration and improved process conditions.

PS-MoP20 Effects of N@sub 2@ Additive Gas on Etching Characteristics of Silicon Oxide Layers in F@sub 2@/N@sub 2@/Ar Remote Plasmas*, J.Y. Hwang,* *D.J. Kim,* Sungkyunkwan University, South Korea*; N.-E. Lee,* Sungkyunkwan University, South Korea, Korea*; C.Y. Jang, G.H. Bae,* ATTO, Korea

In this study, remote plasma etching characteristics of silicon oxide layers were investigated in F@sub 2@/Ar and F@sub 2@/N@sub 2@/Ar plasmas. A toroidal-type remote plasma source was used for the generation of remote plasmas. The effect of additive N@sub 2@ gas on the etch rates of various silicon oxide layers, including PE-oxide (deposited by PECVD using SiH@sub 4@ and N@sub 2@O), O@sub 3@-TEOS oxide (deposited by thermal CVD using ozone and TEOS precursor) and BPSG (borophosphosilicate glass), was investigated by varying the various process parameters, such as the additive gas N@sub 2@ flow rate and the substrate temperature. The species emitted during cleaning were monitored by Fourier transformed infrared spectroscopy (FT-IR) and residual gas analysis (RGA). The etching rate of the silicon oxide layers is increased 20~25% by adding N@sub 2@ gases to the optimized F@sub 2@/Ar chemistry. Under the current experimental conditions, the largest increase in the etch rate of the silicon oxide layers was observed at the flow condition of F@sub 2@:N@sub 2@=2:1. The etch rates of the silicon oxide layers were increased by the factors of 8.7, 8.3, and 35.7 for PE-oxide, O@sub 3@-TEOS oxide, and BPSG, respectively, at the conditions of F@sub 2@(1500 sccm)/N@sub 2@(750 sccm)/Ar (500 sccm) as the substrate temperature increases from 25 to 350°C. The additive N@sub 2@ flow rate and the substrate temperature were found to be the most critical parameters in determining the etch rate of the silicon oxide layers.

PS-MoP21 Comparison of C@sub 4@F@sub 6@ with C@sub 4@F@sub 8@ Chemistry for Deformation of ArF Photoresist and Silicon Dioxide Etching using Dual Frequency Superimposed (DFS) Capacitive Coupled Plasmas*, C.H. Lee,* *C.H. Park, N.-E. Lee,* Sungkyunkwan University, Korea

As the critical dimension (CD) of advanced CMOS devices is scaled down below 100 nm, 193 nm ArF photoresist (PR) needs to be used as a mask for various etching processes including silicon nitride (SiN) hard-mask opening. Recently, dielectric etch process using ArF photoresist mask by dual frequency superimposed (DFS) capacitive coupled plasma (CCP) has attracted a lot of attention. High frequency (HF) power is used to enhance plasma density and low frequency (LF) power is used to control ion bombardment to the wafer. During dielectrics etch process using DFS-CCP, understanding of ArF photoresist deformation is very important. It has been found that the most serious problems of the hard-mask open process with ArF PR are striation, wiggling, and agglomeration of the PR. In this study, we investigated deformation of ArF photoresists and silicon dioxide etching by varying the process parameters such as HF(13.56, 27.12, and 60 MHz)/LF(2 MHz) power ratio, O@sub 2@ flow, CH@sub 2@F@sub 2@ flow rate and etch chemistry (C@sub 4@F@sub 8@ or C@sub 4@F@sub 6@/ CH@sub 2@F@sub 2@/ O@sub 2@/ Ar). Characterization of surface chemical change was performed by X-ray photoelectron spectroscopy (XPS). Surface morphological changes also investigated by field emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM). Also, morphological changes of surface and line edges in ArF PR, SiO@sub 2@ etch rate, selectivity over PR during etching of ArF PR/BARC/SiO@sub 2@ structures were investigated. Effects of process parameters on the etch results will be discussed in detail.

PS-MoP22 Influence of the Positive Ion Composition on the Ion-Assisted Chemical Etch Rate of SrTiO@sub 3@ Thin Films in Ar/SF@sub 6@ Plasmas*, O. Langlois, L. Stafford,* ***J. Margot,*** Universite de Montreal, Canada*; M. Gaidi, M. Chaker,* INRS-Energie, Materiaux et Telecommunications, Canada

The control of the etch rate is one of the critical issues related to the patterning of functional thin films relevant for applications in electronic, opto-electronic and optical integrated devices. This etch rate is known to be strongly influenced by the reactive neutral and total positive ion density, by the positive ion energy, and by the surface temperature. For plasmas sustained in molecular gases such as BCl@sub 3@, CF@sub 4@, C@sub 4@F@sub 8@, and SF@sub 6@, more than one positive ion species can be present simultaneously in the plasma. It is therefore likely that in addition to the previous parameters, the relative concentration of each positive ion species somewhat impacts the etch rate. In this work, we investigate the influence of the positive ion composition on the ion-assisted chemical etch rate of strontium-titanate-oxide (SrTiO@sub 3@) thin films in Ar/SF@sub 6@ plasmas, using a parametric approach. In this context, we characterize the influence of the operating parameters (e.g. gas pressure and absorbed power) on the positive ion density of each charged species by using plasma sampling mass spectrometry and Langmuir probes. It is found that as either the gas pressure increases or the absorbed power decreases, the relative concentration of molecular positive ion species such as SF@sub 3@@super +@ and SF@sub 5@@super +@ strongly increase. Based on these results, it is possible to define an effective positive ion mass M that describes the overall positive ion composition of the plasma. The SrTiO@sub 3@ etch yield Y (i.e. the number of atoms desorbed from the surface per incident ion) is shown to be a decreasing function of the effective ion mass M, in excellent agreement with the predictions of a simple ion-assisted chemical etching model.

PS-MoP23 In Situ Etching of (Pb,Sr)TiO@sub 3@ Thin Films by using Inductively Coupled Plasma*,* ***G.H. Kim,*** *K.T. Kim, C.I. Kim,* Chungang University, Korea

To overcome the limitations of conventional capacitor structure, high-k material, for example, (Ba,Sr)TiO@sub 3@ (BST) and (Pb,Sr)TiO@sub 3@ (PST), have been intensively studied for a number of integrated devices such as dynamic random access memories (DRAM) because high dielectric constant, lower crystallization temperature and low leakage current. However, BST thin film possesses a satisfactorily characteristics, it was known that a post heat treatment at a high temperature was essential to obtain good electrical property. The heat treatment at high temperature can cause deleterious effects on an electrode, barrier metal, and contact plug. On the other hand, PST thin film can be a promising material due to its high dielectric constant, paraelectricity at normal operating temperature and good electrical properties. In this study, inductively coupled plasma etching system was used for PST thin film etching. The chlorine base plasmas were characterized by optical emission spectroscopy (OES), Langmuir probe and quadrupole mass spectrometer (QMS) analysis. OES and QMS were used for the analysis of byproduct.

PS-MoP24 Surface Etching Mechanism of Bi@sub 4-x@La@sub x@Ti@sub 3@O@sub 12@ Thin Films using Quadrupole Mass Spectroscopy and X-ray Photoelectron Spectroscopy*,* ***J.G. Kim,*** *G.H. Kim, K.T. Kim, C.I. Kim,* Chungang University, Korea

Ferroelectric thin films are employed for ferroelectric random access memories (FeRAMs). FeRAMs offer non-volatility, a lower voltage operation and larger write cycle numbers. (Bi@sub 4-x@La@sub x@)Ti@sub 3@O@sub 12@ (BLT) thin films was proposed as a promising ferroelectric material that does not exhibit the polarization fatigue, does have bigger remanent polarization value than that of SrBi@sub 2@Ta@sub 2@O@sub 9@. Accordingly, for high density FeRAMs, the etching mechanism of BLT thin films must be understood by investigation of both chemical and physical reactions between plasma species and BLT thin films. In this paper, the etching properties of BLT thin films in inductively coupled Ar/Cl@sub 2@ plasma was investigated with various gas mixing ratio. For investigation of chemical reaction with ions and radicals, in-situ monitoring using quadrupole mass spectroscopy (QMS) with 250µm orifice was performed. After etching process, etched BLT thin film surface was analyzed with X-ray photoelectron spectroscopy (XPS), since etching byproducts of BLT thin films has non-volatile species and re-deposited its surface. One could explain how to react the ions and radicals on the surface of BLT thin films to combine the QMS scanning data and the analyzed data of XPS spectrum.

PS-MoP25 The Etching Characteristics of LaNiO@sub 3@ Thin Films in CF@sub 4@/Cl@sub 2@/Ar and BCl@sub 3@/Cl@sub 2@/Ar Gas Chemistry*, G.H. Kim, K.T. Kim,* ***C.I. Kim,*** Chungang University, Korea*; D.P. Kim,* KDG Engineering Co., Ltd., Korea*; C.I. Lee,* Ansan College of Technology, Korea*; T.H. Kim,* Yeojoo Technical College, Korea

During the last decade, ferroelectric thin films have been attracting much attention for nonvolatile memory application. Among ferroelectric material, zirconate titanate (Pb(Zr,Ti)O@sub 3@ : PZT) thin films have been studied extensively because PZT has high dielectric constant and bistable polarization. Platinum (Pt) film usually employed as an electrode for metal-ferroelectric-metal (MFM) capacitor for 1 transistor-1 capacitor structure (1T/1C). However, Pt/PZT/Pt capacitors suffer from poor resistance on fatigue property due to generation oxygen vacancies in interface of Pt/PZT during exposing to a hydrogen environment. Therefore, metal-oxides (IrO@sub 2@ and RuO@sub 2@) have been studied for top electrode. However, IrO@sub 2@ and RuO@sub 2@ have the problems that metal-oxides are easily transferred to metallic Ir and Ru under vacuum and high temperature conditions, resulting in degradation of ferroelectric properties by H@sub 2@ diffusion. Recently, LaNiO@sub 3@ (LNO) electrodes are challenged as top and bottom electrodes. Because LNO has a pseudo cubic perovskite structure, the close lattice constant (3.84 Å) to PZT (4.04 Å) and a good metallic property. In order to realize highly integrated FRAMs, the etching process must be developed. In this case, the task of primary importance is to understand etching mechanism to open the ways for the optimization of etching process. Unfortunately, there is only one report for etching LNO thin film. Therefore, the etching mechanism of LNO films should be understood in terms of etching system and gas mixture. In this work, we investigated etching characteristics and mechanisms of LNO thin films using CF@sub 4@/Cl@sub 2@/Ar and BCl@sub 3@/Cl@sub 2@/Ar mixtures in inductive coupled plasma (ICP) system. Plasma diagnostic was represented by quadrupole mass spectrometer and Langmuir probes measurements.

PS-MoP26 Low Damage Etching of III-V Semiconductors using a Low Angle Forward Reflected Neutral Beam*,* ***B.J. Park,*** *K.S. Min, H.C. Lee, J.W. Bae, G.Y. Yeom,* Sungkyunkwan University, Korea

Plasma etching is essential in the fabrication of compound semiconductor devices due to the requirements of anisotropic profiles and submicron features for optoelectronic integrated circuits, microwave devices, lasers, etc. Any process-related damage such as electrical damage and surface modification remaining during the processing may cause serious problems due to the size limitation of the devices. Therefore, etch processes without or negligible damages are required. In this study, fluorine based directional neutral beams were formed by low angle reflection of the energetic directional fluorine-based reactive ion beams generated by a fluorine-based inductively coupled plasma (ICP) gun. GaAs and GaN were etched and their etch characteristics such as etch rates and etch damage due to the etching were investigated. As a comparison, GaAs and GaN were etched by a conventional ICP and their damage characteristics were compared. When dry etch damage of the etched GaAs and GaN were investigated using PL and PRS, no damage could be observed when the neutral beam etching was used while the GaAs and GaN etched by the ICP showed significant surface damage. No damage by the energetic neutral beam etching appears to be related to the insignificant reaction of the neutrals with the electrically active surface states during the etching.

Surface Science
Room Exhibit Hall C&D - Session SS-MoP
Surface Science Poster Session

SS-MoP2 Probing the Vibrational State-Resolved Gas-Surface Dynamics of CH@sub 4@ (@nu@@sub 4@,v=1) on Ni(111)*,* ***V. Campbell,*** Tufts University

We describe an experimental approach that yields vibrational-state-resolved reaction probabilities for polyatomic molecules without the need for selective laser excitation of the target state. The method relies on a detailed knowledge of the vibrational structure of the molecule under study and its vibrational energy transfer dynamics in a supersonic expansion. In the case of methane, non-equilibrium cooling of vibrational states within polyads leads to the population of a single vibrationally excited state under easily obtained expansion conditions, even though several excited vibrational states would contain significant population under the nominal thermal conditions of the nozzle source. We apply this approach to extract state-resolved reaction probabilities for methane in the @nu@@sub 4@ vibrational fundamental and incident on clean Ni (111) surface. State-resolved reaction probabilities obtained in this way are free from the vibrational-state averaging that clouds interpretation of beam-surface reactivity measurements and permit a more direct test of theoretical models of gas-surface reactivity.

SS-MoP3 Alkylidene Functionalization of Molybdenum Carbide Surfaces: Thermal Stability and Chemical Reactivity*, H. Oudghiri-Hassani, M. Siaj,* ***I. Temprano****, C. Maltais, P.H. McBreen,* Université Laval, Canada

Metal carbides possess a blend of metallic and ceramic properties and are amenable to unique surface modification procedures. In particular, molybdenum carbide surfaces may be functionalized using alkylidene groups. Such groups involve a double bond between the organic component and a single molybdenum atom at the surface, as distinct from bridge-bonded structures. We have previously shown that surface alkylidenes on molybdenum carbide display anomalously high thermal stability. The origins of this thermal stability will be discussed on the basis of extensive synchrotron photoemission, RAIRS and isotope substitution desorption data. The combined data reveal a key role for excess surface carbon in stabilizing the alkylidene groups to temperatures as high as 900 K. Furthermore, it will be shown that the metathesis activity of the surface alkylidene initiating sites may be used to perform add-on functionalization using a variety of olefins and substituted olefins.

SS-MoP4 Sulfur-CO Interactions on Cu(100) Films through Surface Resistivity and Infrared Reflectance Measurements*,* ***C. Liu****, R.G. Tobin,* Tufts University

Interactions between dissimilar adsorbates on Cu(100) thin films have been investigated experimentally through their effects on electrical transport in the metal. We report measurements of surface resisitivity induced by CO on 50 nm-thick epitaxial Cu(100) films preadsorbed with different amounts of sulfur, together with temperature-programmed desorption (TPD) and infrared reflectance measurements. Adsorbate-induced surface resistivity arises from the scattering of conduction electrons in the metal from the impurity potential created by the adsorbate. Previous experiments have shown that the scattering cross section of sulfur decreases with increasing coverage, indicating a strong sulfur-sulfur interaction.@footnote 1@ In the present work, sulfur-CO interactions are explored by measuring the slope of the resistivity vs. CO coverage curve as a function of sulfur precoverage. Effects of sulfur on CO's scattering cross section are revealed as changes in the slope. Sulfur-induced changes in CO adsorption are also monitored with infrared vibrational spectroscopy and TPD. @FootnoteText@ @footnote 1@R.G. Tobin, Surf. Sci. 524, 183 (2003).

SS-MoP5 Adsorption Geometries of Prochiral Molecules on Pt(111): Heterogeneous Enantioselective Hydrogenation*,* ***M.A. Laliberté****, A. Rouffignat, I. Temprano, S. Lavoie, P.H. McBreen,* Université Laval, Canada

HREELS and RAIRS were used study the adsorption of carbonyls and dicarbonyls on Pt(111) with the goal of better understanding the Orito reaction. The Orito reaction describes the enantioselective hydrogenation of the keto-function of alpha-ketoesters on chiral-modified platinum particles. Measurements were performed on acetone, ethyl formate,biacetyl, methyl pyruvate and ethyl pyruvate adsorbed on clean Pt(111), and coadsorbed with toluene, benzene, naphthalene, methyl naphthylene, cyclohexane and naphthylethylamine. Very strong coadsorption interactions resulting in complete modification of the adsorption geometries of the carbonyl molecules were observed for several of these systems. The results aid in mapping out the range of adsorption geometries available to dicarbonyl substrates in the Orito reaction. The results will be discussed in the context of a proposed new mechanism for the enantioselective reaction.

SS-MoP6 "Hot Electrons" at Organic-Metal Interface: Photodissociation of Phenol on Ag(111)*,* ***S. Ryu****, J. Chang, S.K. Kim,* Seoul National University, Korea

Photodissociation of many organic adsorbates on metal surfaces has been attributed to photoexcited "hot electrons". To address this issue, we have explored the interfacial electronic structure of phenol adsorbed on Ag(111) using time-resolved two-photon photoemission spectroscopy. The photoinduced anion state of phenol was found at 3.1 eV above the Fermi level at one monolayer coverage. The binding energy of this state remained constant at around 0.7 ~ 0.8 eV for all coverages. Polarization dependence of the photoelectron signal revealed mechanistic details for each excitation step. The lifetime of the anion state was found to increase from 33 to 60 fs, indicating its lesser coupling to the bulk as the coverage increased from 1 to 9 ML. These findings demonstrate the role of hot electrons in photodissociation of adsorbates.

SS-MoP7 Interaction of Sulphur-Containing Anions with Copper Single Crystal Electrodes*, J. Hommrich, S. Hümann, P. Broekmann, K. Wandelt,* ***A. Spänig****,* University of Bonn, Germany

Processes at metal/electrolyte interfaces are a promising route to modify and structure surfaces on the nanometer scale. This, because processes at metal/electrolyte interfaces may be easier to control than those in vacuum, and are probably more economic. In this contribution we summarize results for sulphur-containing anion adsorption from solution on single crystal copper electrodes as obtained with in-situ ElectroChemical Scanning Tunneling Microscopy (ECSTM) and Fourier-Transform Infrared Spectroscopy (FTIRS) in combination with ex-situ surface analytical methods like AES, LEED, XPS, ISS etc. Hetero-atoms like, for instance, sulphur are often the anchors through which organic molecules are bound to surfaces. In particular, results will be presented and discusses for the most basic anionic groups, namely SO@sub 4@@super 2-@ and S@super 2-@, as well as derivatives thereof like sulfonate and thiocyanate anions on Cu(111) and Cu(100) electrodes. Special emphasis will be placed on the adsorbate structure and dynamics, on structural phase transitions, adsorption induced surface reconstruction as well as chemical stability as a function of electrode potential.

SS-MoP8 Electrochemical Formation of a Semiconducting Metal Oxide observed by In Situ Tunneling Spectroscopy*,* ***I. Diez-Perez****, A. Guell,* University of Barcelona, Spain*; P. Gorostiza,* University of California, Berkeley*; F. Sanz,* University of Barcelona, Spain

Obtaining tunneling spectroscopic data in electrolytic solutions is fundamental to understand electrode reactivity.Electrochemical scanning tunneling spectroscopy(ECTS) represents a powerful method for the in situ elucidation of the electronic structure on solid-electrolyte interfaces.Its experimental realization has been reported only in a few instances with some limitations.@footnote 1@ We present tunneling spectra of an Fe electrode immersed in a borate buffer electrolyte while it is reversibly oxidized to different potentials within the three oxidation ranges:Fe(0),Fe(II) and Fe(III).@footnote 2@ Complete series of ECTSpectra within the entire Fe passivation range allow us the representation of oxide surface conductograms by plotting the e- energy level on the Y-axis(tip potential),the electrode oxidation state on the X-axis(sample potential) and surface conductance represented by the Z gray scale.Our spectra span up to 2.2V using high tip potential scan rates(up to 15V/s).We have developed a new method to prepare and isolate Pt/Ir tips specially for in situ STS applications.@footnote 3@ Under conditions where the passive film is chemically stable in the working buffer,we found that the different redox transitions at the iron surface result from the availability of free charge carriers controlled by electron energy barriers at the oxide/solution interface.The passivity of iron results from the build-up of an energy barrier in n-Fe(III) and the absence of states available for charge exchange within almost 1.5eV below the CB edge.Increasing the sample potential in the passive plateau results mostly in increasing the band bending inside the oxide and decreasing the electron concentration. @FootnoteText@ @footnote 1@E.Tomita,N.Matsuda,K.Itaya,J.Vac.Sci.Technol.,A8(1)534(1990).@footnote 2@I.Diez-Perez,P.Gorostiza,F.Sanz.J.Electrochem.Soc.,150:B348(2003).@footnote 3@A.G.Guell,I.Diez-Perez,P.Gorostiza,F.Sanz, Anal Chem.,76,5218.(2004).

SS-MoP9 Interaction of Water Vapor with Clean and Contaminated Ru Surfaces*,* ***B.V. Yakshinskiy****, N.S. Faradzhev, T. Graber, T.E. Madey,* Rutgers, The State University of New Jersey

We compare the interaction of water vapor (H@sub 2@O and D@sub 2@O) with two important surfaces of hcp Ru: the atomically-rough (10-10) and the smooth close-packed (0001) surfaces. Several methods, including temperature programmed desorption (TPD), x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and low energy ion scattering (LEIS) were used to study adsorption/desorption processes of water on the clean surfaces, as well as on carbon-dosed, oxygen-dosed and air-exposed surfaces. Both H@sub 2@O and D@sub 2@O undergo partial dissociation upon adsorption/desorption on Ru(10-10), which is in contrast to Ru(0001), where there is a striking isotope effect: D@sub 2@O is adsorbed molecularly, without dissociation, whereas H@sub 2@O dissociates partially. The data show non-wetting behavior of water on the air-exposed or the carbon-covered surfaces, but water becomes more strongly bonded to an oxygen-dosed substrate. We also report on the electron-induced dissociation and the electron-stimulated desorption (ESD) of water adsorbed on these surfaces at low temperature. The data provide insights into recent controversy concerning the interaction of water with Ru surfaces.

SS-MoP10 XPS and Sulfur K-edge NEXAFS Characterization of Isotope Effect for Coadsorption Systems (H@sub 2@O or D@sub 2@O)/L-Cysteine/Cu(100)*, **S. Yagi**, D. Tomihara, T. Nomoto,* Nagoya University, Japan*; G. Kutluk,* JST, Japan*; M. Taniguchi,* Hiroshima University, Japan*; K. Soda,* Nagoya University, Japan

Adsorption structure and chemical property of a sulfur-containing amino acid molecule of L-Cysteine on transition metal surface has been interested in a bio-compatibility, a bio-catalysis and a bio-materials fields. XPS (X-ray Photoelectron Spectroscopy) and NEXAFS (Near edge X-ray Absorption Fine Structure) techniques have established themselves as a powerful tool to characterize both a local molecular adsorption structure and a chemical condition of the adsorbates at adsorption sites. In the present study, we have paid attention to the isotope effect for coadsorption systems (H@sub 2@O or D@sub 2@O)/L-Cysteine/Cu(100) studied by coupling of (S2p, C1s, O1s and N1s) XPS and sulfur K-edge NEXAFS measurements. There are some dominant differences in the experimental results of XPS and NEXAFS spectra for coadsorption systems of (H@sub 2@O or D@sub 2@O)/L-Cysteine/Cu(100).

SS-MoP11 Covalent Attachment of Pt-Dendrimer Encapsulated Nanoparticles to 11-Mercaptoundecanoic Acid Thin Films*, T.J. Black, K.A. Perrine, Y. Gu, H.J. Ploehn, **D.A. Chen**,* University of South Carolina

Polyamidoamine dendrimers represent a diverse tool for chemical and biological research due to their functionality and highly tunable properties. The work presented here takes advantage of the dendrimer's ability to act as a nanoscale template for controlling the size distribution of metal particles formed in solution. Specifically, amine-terminated, generation 4 polyamidoamine dendrimers (G4-NH@sub 2@) are treated with K@sub 2@PtCl@sub 4@ in a metal:dendrimer ratio of 40:1 to coordinate approximately 40 Pt@super 2+@ ions inside each dendrimer. Subsequent reduction with NaBH@sub 4@ is believed to form metallic Pt particles ~2 nm in diameter according to transmission electron microscopy studies. We have optimized a procedure that covalently links the dendrimer encapsulated nanoparticles onto a self-assembled monolayer of 11-mercaptoundecanoic acid (MUA) on Au(111) surfaces; this robust dendrimer film allows for various mechanical and chemical treatments that would not otherwise be possible. After the MUA monolayer is exposed to EDC (1-[3-(diethylamino)propyl]-3-ethylcarbodiimide hydrochloride) and an NHS (hydroxysuccinic acid)catalyst followed by treatment with the dendrimer solution, infrared reflection absorption spectroscopy (IRAS) experiments suggest that amide bonds are formed between the SAMs and the dendrimer by the disappearance of the carboxylic acid mode at 1722 cm@super -1@ from the MUA accompanied by the appearance of amide modes at 1670 cm@super -1@ and 1556 cm@super -1@. X-ray photoelectron spectroscopy also confirmed the presence of Pt-G4NH@sub 2@ on the SAMs since nitrogen and platinum signals were detected. The next step of this project will be to remove the dendrimer templates and SAM from the Au(111) surface by oxidation-reduction cycles, leaving behind the Pt nanoparticles. The ultimate goal of this work is to study the surface chemistry of the supported, well-characterized Pt particles in model catalytic reactions, such as CO oxidation.

SS-MoP12 Adsorption and Hydrogenation of 1,3-butadiene on Pd(111) and Pd-Sn/Pd(111) Surface Alloys*, **Chr. Breinlich**, J. Haubrich, C. Becker, K. Wandelt,* University of Bonn, Germany

The selective hydrogenation of dienes into mono-olefines is an important industrial reaction. Industrial processes are usually carried out with supported catalysts containing transition metals such as palladium or platinum. Palladium shows a high activity and selectivity for these reactions. Therefore we have studied the adsorption and hydrogenation of 1,3-butadiene on Pd(111) and Sn-modified Pd(111) surfaces. The Pd-Sn surface alloys were produced by annealing of tin layers of various thicknesses. Depending on the amount of deposited tin this procedure actually resulted in ordered surface alloys of (@sr@3x@sr@3)R30° or p(2x2) superstructure, which were characterized by LEED, AES and UPS. The adsorption and reaction of 1,3-butadiene was investigated by TPD. After 1,3-butadiene adsorption at 55 K the desorption of the multilayer was found near 120 K on all surfaces. Further heating lead to the complete dehydrogenation of the butadiene on the Pd(111) surface. On the surface alloys only a part of the butadiene dehydrogenates while the rest desorbs at 200 - 230 K. By preadsorbing either hydrogen or deuterium the 1,3-butadiene can be partially hydrogenated to butene on the surface alloys. The partial hydrogenation is highly selective since no desorption of butane has been found. The branching ratio of desorption vs. hydrogenation on the surface alloys is clearly a function of the amount of tin, which was deposited and, hence, the surface stoichiometry. HREELS investigations reveal the adsorption modes of 1,3-butadiene and butene on these surfaces.

SS-MoP13 Oxygen-induced Faceting of NiAl(111)*, **E. Loginova**, W. Chen, N.M. Jisrawi, T.E. Madey,* Rutgers University

We report the adsorption of oxygen and oxygen-induced faceting of NiAl(111), as studied by means of LEED, AES and high-resolution soft XPS(HRSXPS, using synchrotron radiation at NSLS). The atomically rough NiAl(111) surface remains planar at room temperature when exposed to oxygen. However, the surface changes its morphology and becomes faceted upon annealing at 1100K and higher; nucleation and growth of facets are studied. The adsorption and reaction of oxygen are characterized by HRSXPS measurements of Al 2p and Ni 3p core levels for the faceted and planar surfaces. The data indicate that a well-ordered thin aluminum oxide film can be formed on the faceted NiAl surface. Our work is motivated by the possibilty that self-organized alumina thin-film-covered NiAl facets might be used as templates for uniform growth of metallic nanostructures with controlled size and spacing. The Al@sub 2@O@sub 3@/NiAl(111) system is a good model material for studying catalytic reactions over Al@sub 2@O@sub 3@-supported metal catalysts.

SS-MoP14 Adsorption of Sulfur Dioxide on Zircaloy-4*, **N. Stojilovic**, R.D. Ramsier,* The University of Akron

The adsorption of sulfur dioxide on Zircaloy-4 surfaces is investigated using Auger electron spectroscopy. We find that both surface oxidation and saturation with sulfur and oxygen occur at low coverages at 300 K. Heating above 800 K results in oxygen dissolution into the bulk whereas sulfur stays in the near surface region. We examine effects of this residual sulfur on subsequent sulfur dioxide and oxygen adsorption. In both cases the adsorbates oxidize the sulfur-contaminated surface. Sulfur dioxide exposures at 300, 600 and 900 K all result in similar amounts of surface sulfur, indicating similar sticking coefficients in this temperature range. However, 900 K adsorption does not result in a shift of the Zr(MNN) feature that would signify surface oxidation. Thus this system can either adsorb or absorb oxygen from sulfur dioxide depending on the temperature, and the sulfur remains trapped near the surface without poisoning it with respect to subsequent oxidation.

SS-MoP15 Surface and Bulk Electronic Structures of Heusler-type Fe@sub 2@VAl*, **M. Miyzaki**, K. Soda, S. Yagi, M. Kato, T. Takeuchi,* Nagoya University, Japan*; U. Mizutani,* Toyota Physical and Chemical Research Institute, Japan*; Y. Nishino,* Nagoya Institute of Technology, Japan

Surface and bulk electronic structures of Heusler-type Fe@sub 2@Al have been studied by both surface- and bulk-sensitive photoelectron spectroscopy, in particular, for the valence band and V 2p core level regions, in order to elucidate the changes in the valence band electronic structures for the surface and bulk regions and to clarify the mechanisms of its unusual transport properties@footnote 1@ and of the large enhancement of its thermoelectric power on a small deviation in the chemical composition.@footnote 2@ The valence band spectrum reveals fairly large intensity at the Fermi level E@sub F@ for the surface-sensitive low photon energy excitation but considerably small E@sub F@ intensity for the bulk-sensitive high photon energy excitation. This intensity reduction implies that a pseudogap is formed around E@sub F@ in the bulk electronic structure, as predicted by band calculations.@footnote 2@ The intensity between the binding energy of 0.4 eV and E@sub F@ is relatively increased for the large photoelectron takeoff angle (measured from the surface normal). These facts indicate that the pseudogap is destroyed in the surface layers. The V 2p core level spectrum shows a surface-derived satellite structure in the low binding energy side of the main bulk band. This suggests that the valence electron concentration around V may be large in the surface region in comparison to the bulk. We will discuss the surface and bulk electronic structures with use of a DV-X@alpha@ local electronic structure calculation. @FootnoteText@ @footnote 1@ Y. Nishino et al., Phys. Rev. B71, 094425 (2005).@footnote 2@ Y. Nishino, Materials Trans. 42, 902 (2001).

SS-MoP16 Growth and Oxidation of Ultrathin Films of Zirconium on the Au(111) Surface*, T.J.Z. Stock,* Queen's University, Canada*; **A.J. Slavin,*** Trent University, Canada

The growth and oxidation of ultrathin zirconium films (to 5 atomic layers) on the gold(111) surface in ultrahigh vacuum have been studied as a function of substrate temperature and oxygen pressure. The oxide films are of interest as a possible replacement for SiO@sub2@ in the gate of field-effect transistors. The study has used Auger electron spectroscopy, electron energy-loss spectroscopy, low energy electron diffraction and work function measurements. The evolution of the chemical composition of the oxide layer has been followed using a high-stability quartz-crystal microbalance.@footnote 1@ @FootnoteText@ @footnote1@ L. Bouzidi, S.S. Narine, K.G. Stefanov and A.J. Slavin; A high-stability quartz-crystal microbalance for investigations in surface science. Rev. Sci. Instrum. 74, 3039-3044 (2003).

SS-MoP17 Adsorption of Acetic Acid on Zn@sub x@Ni@sub 1-x@ O*, **H.G. García Flores,*** University of Nebraska-Lincoln and Los Alamos National Laboratory*; A. Starace, M.A. Langell,* University of Nebraska-Lincoln

Zinc can be dissolved in rocksalt NiO to produce solid solutions of Zn@sub x@Ni@sub 1-x@ O over an approximate composition range of 0 @<=@ x @<=@ 0.35. Both metals are formally M @super 2+@, typically the stable oxidation state in oxides, but the octahedral coordination site of the cations in the rocksalt structure is unusual for zinc, which is typically tetrahedral as is found in wurtzite ZnO. The unique chemical environment of the zinc-nickel oxide solid solution can potentially result in new and interesting surface reactivity. Solid solutions of the zinc-nickel oxide over the range of 0.05 @<=@ Zn @<=@ 0.35 were prepared by calcination at 1200 K and were characterized using powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Auger electron spectroscopy (AES). The Auger parameter for zinc in these homogeneous solid solutions increases indicating stronger ionic character. Acetic acid (CH@sub 3@COOH) was then used to examine the surface reactivity of the mixed-metal solid solution in a series of adsorption experiments that were carried out as a function of zinc concentration and surface pretreatment. At 250 K, the primary adsobate observed is bidentate acetate and, once formed, the species is stable on the substrate to approximately 500 K.

SS-MoP18 Adsorption and Reaction of CO and CO2 on Oxidized and Reduced SrTiO3(100) Surfaces*, **L. Wang**,* Pacific Northwest National Laboratory*; S. Azad,* Rice University*; M.H. Engelhard,* Pacific Northwest National Laboratory

The adsorption and reaction of CO and CO2 on oxidized and reduced SrTiO3(100) surfaces have been studied using temperature programmed desorption (TPD) and x-ray photoelectron spectroscopy (XPS). XPS results indicate that the oxidized SrTiO3(100) surfaces are nearly defect-free with predominantly Ti4+ ions whereas the sputter-reduced surfaces contain substantial amounts of defects. Both CO and CO2 are found to adsorb weakly on the oxidized SrTiO3(100) surfaces. The desorption activation energies of CO and CO2 from the oxidized SrTiO3(100) surfaces are 38 and 32 kJmol-1, respectively, following adsorption at 110 K. On sputter-reduced surfaces, enhanced reactivity of CO and CO2 is observed due to the presence of oxygen vacancy sites that are responsible for dissociative adsorption of these molecules. Our studies indicate that CO and CO2 molecules exhibit relatively weaker binding to SrTiO3(100) compared with TiO2(110) and TiO2(100) surfaces. These differences can be attributed primarily to the influence of the Sr cations on the electronic structure of the Ti cations in the mixed oxide of SrTiO3.

SS-MoP19 Molecular Dynamics Study of the Aluminum/ @alpha@-Alumina Interface Using an Efficient Charge-Transfer Potential*, **B.D. Devine,*** University of Florida*; A.J.H. McGaughey,* University of Pittsburgh*; S.B. Sinnott, S.R. Phillpot,* University of Florida

Many of the properties that make aluminum a desirable commercial material are attributable to it rapidly forming a passivating oxide layer. In studying the properties of such active metals, the nucleation of the oxide phase, its structural evolution, and the resulting interfacial effects must be considered. Mechanistic exploration of oxide formation is challenging at the atomistic level due to length and time scale limitations, and the complexity of simultaneously modeling a metal and its oxide. Here, the aluminum/@alpha@-alumina interface is investigated using classical molecular dynamics simulations. The empirical, charge-transfer Streitz-Mintmire@footnote 1@ potential is coupled with an efficient direct pair-wise summation of the Coulombic interactions.@footnote 2@ The merits of the computational approach will be critically evaluated with the intent of applying the techniques to a large scale MD simulation of oxide formation and microstructure evolution. This work is supported by the National Science Foundation (grant no. DMR-0426870). @FootnoteText@@footnote 1@Streitz, F., Mintmire, J, Phys Rev. B 1994, 50, 996 @footnote 2@Wolf et al., J. Chem. Phys.1999, 110, 8254 .

SS-MoP21 Investigation of sp@super 2@ Carbon in Nanodiamond*, **J. Hu,** J. Foord,* University of Oxford, UK, United Kingdom

Diamond electrodes have wide application in electroanalysis, electrolysis, waste water treatment etc. due to superior properties, such as chemical inertness, high overvoltage, and resist to electrode fouling. The sp@super 2@ carbon inclusion in microcrystalline and nanodiamond is believed to make a major contribution to the performance of diamond electrodes. We investigate this in the present paper. Microcrystalline and nanodiamond films are grown on Si (100) and polished Ti sheet with different methane concentrations by MWCVD. The samples are characterized by Raman Spectroscopy, SEM, XPS, Voltammetry and conductivity. With increasing concentration of methane from 1% to 4 %, the grain size decreases slightly and becomes more homogeneous. With further higher concentration of methane, the samples are nanocrystalline with typical grains of around 200 nm. XPS and EELS indicate that only a trace amount of sp@super 2@ carbon is present on sample surface. About 1% percent of sp@super 2@ carbon in microcrystalline diamond is etched away in electrochemical polarization at 2.2V in 1M HNO@sub 3@ solution, and more sp@super 2@ carbon can be etched away for nanodiamond. This shows that most of the sp@super 2@ carbon inclusions are present in grain boundaries instead of embedded into diamond grains or present as graphite grains at the electrode surface. Electrochemical etching protocols are examined, to minimize unwanted effect of sp@super 2@ carbon on the performance of diamond electrode.

SS-MoP22 Imaging the Structure of Natural Organic Matter Adsorbed onto Carbonaceous Surfaces with Atomic Force Microscopy*, **J. Gorham**, H. Fairbrother,* Johns Hopkins University

Developing a microscopic understanding of the adsorbate layers formed by Natural Organic Matter (NOM) on carbonaceous surfaces is useful in developing more realistic models under environmental conditions. This information could also have important technological ramifications for water treatment strategies where NOM reduces the adsorptive capacity of activated carbons. In this study, the adsorption of NOM (obtained from the Great Dismal Swamp, VA) on Highly Ordered Pyrolytic Graphite (HOPG) has been studied at the liquid-solid interface using Atomic Force Microscopy (AFM). In these studies HOPG was used to model the extended graphene sheets that characterize the exposed surface of activated carbons. Under low pH conditions (pH 4.0), NOM particles were observed to cover the entire HOPG surface with a layer thickness of ~2 nm. Evidence of ordered adsorbate structures involving NOM were observed at low pH. As the pH of the NOM solution increased, the surface concentration of NOM decreased systematically; at pH 10, <10% of the HOPG was covered by adsorbed NOM. Particle size was also influenced by pH with the average size of adsorbed structures being greater at higher pH. The structure of adsorbed NOM was significantly modified by drying with "ring like" structures and larger NOM aggregates observed. Results will also be presented on the effect of ionic strength on the structure of the adsorbate layer.

SS-MoP23 Selective Reduction of MoO@sub 3@ Nanostructures on Au(111)*, **D.S. Pinnaduwage**, X. Deng, M.M. Biener, C.M. Friend,* Harvard University

Well-ordered MoO@sub 3@ nanostructures on Au(111) have been prepared using iterative dosing of Mo(CO)@sub 6@ and NO@sub 2@. A c(4x2) unit cell is observed for these nanostructures in scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). The presence of Mo@super 6+@ is confirmed by X-ray photoelectron spectroscopy (XPS). Selective reduction of MoO@sub 3@ nanostructures has been achieved by annealing at 650 K for varying times. Sheer planes are observed in STM due to the formation of Mo@super 5+@. Based on XPS data, ultimately, thermal reduction results in Mo@super 6+@ and Mo@super 5+@ at a 1:1 ratio on the Au surface. However, Mo@super 4+@ is absent in all thermal treatments, indicating the existence of a kinetic barrier for the reduction of either Mo@super 6+@/Mo@super 5+@ to Mo@super 4+@.

SS-MoP24 LEED and XPS Study of the Oxidation Process on Cu(111)*, **K. Moritani,*** JAERI, Japan*; M. Okada,* Osaka University, Japan*; Y. Teraoka, A. Yoshige,* JAERI, Japan*; T. Kasai,* Osaka University, Japan

The oxidation of Cu has been of great interest because of the important role of Cu oxides in material science. Thus, many experimental and theoretical studies have been performed to understand the oxidation of Cu. However, the oxide-formation processes and the oxygen induced reconstruction on Cu(111) is far less clear. It is advantageous to control oxidation processes and structure in order to understand the chemical reactions and oxide formation processes on the nanoscale. In this work, we studied the oxidation of Cu(111) surface with a hyperthermal O@sub 2@ molecular beam (HOMB) and thermal O@sub 2@ gas using low energy electron diffraction (LEED) and high-resolution X-ray photoemission spectroscopy (XPS) in conjunction with a synchrotron radiation (SR) source. All experiments were performed with the surface reaction analysis apparatus (SUREAC 2000) constructed in BL23SU at SPring-8. The kinetic energy of incident O@sub 2@ can be controlled by changing the O@sub 2@, He and/or Ar gas mixing ratios and the nozzle temperature. After the irradiation of a proper amount of HOMB or thermal O@sub 2@ gas, high-resolution XPS spectra were measured at ~300 K using SR and then LEED pattern was observed. We measured O-uptake curves, determined from the integration of O-1s XPS on the surface, after the HOMB irradiation or the exposure to the oxygen atmosphere. The oxidation with under 0.23 eV HOMB at room temperature saturated at 0.3 ML, when only (1x1) and diffused background LEED pattern was observed. The additional incident energy above 0.5 eV promoted the further oxidation above 0.3 ML and induced the reconstruction to c(8x8) phase where the O-1s peak sifted the low binding energy side. This reconstruction and peak shift were observed after thermal gas exposure at the higher temperature. We discuss possible models of oxidation process on the basis of the incident-energy and temperature dependence of the O-1s XPS spectra and LEED pattern.

SS-MoP26 Computational Study of the Deposition of Metal-Oxide Thin Films*, **J.M. McKillip**, S.R. Phillpot, S.B. Sinnott,* University of Florida

Thin film deposition of SrTiO@sub 3@ is currently a popular area of research due to its widespread use in electronic applications and the motivation to shrink electronic components. Pulsed laser deposition (PLD) is an effective deposition process yielding dense, homogeneous thin films. Here, classical molecular dynamics simulations are used to determine the mechanisms involved in PLD. The simulations show that collisions that occur between the incident particles and the substrate can induce chemical reactions. The simulations consider the deposition of SrO and TiO@sub 2@ molecules with a kinetic energy between .1 and 1 eV/atom on a (001) surface of SrTiO@sub 3@. The effects of impact energy, orientation of incident particles, and surface termination layer (SrO vs. TiO@sub 2@) are examined. The main surface phenomenon of interest is chemical changes that occur at the oxide surface due to the ablating particles. The simulation results are compared to experimental data, where available. This work is supported by the National Science Foundation (DMR-0426870).

SS-MoP29 Chain Structure of Surface Hydroxyl Groups on TiO@sub 2@(110) with Line Oxygen Vacancy Studied by in-situ Noncontact Atomic Force Microscopy (NC-AFM)*, **Y. Namai**, O. Matsuoka,* Mitsui Chemicals, Inc., Japan

Surface hydroxyl groups are essential species in many catalytic reactions. Especially, in oxide surfaces, they play a crucial role in reforming of the surface reactivity due to the adsorption of hydrogen adatoms at oxygen ion (anion) sites. Therefore controlling of the surface hydroxyl on catalysis surfaces is important in the reactivity and the selectivity. As a model surface to control hydroxyl groups, a slightly reduced TiO@sub 2@(110) surface was utilized. By repeating many cleaning cycles, surface oxygen atoms on bridge oxygen rows of the TiO@sub 2@(110) linearly desorbed, and the line vacancy structures were obtained. The line vacancy was formed by increasing of the density of oxygen vacancies on the TiO@sub 2@(110) surface. After exposing H@sub 2@O (1.0 x 10@super -4@ Pa for 120 s), hydroxyl chain structure, which is linearly arranged hydroxyl groups into two rows on bridge oxygen rows, were formed on the TiO@sub 2@(110) surface with the line oxygen vacancy. In-situ NC-AFM measurements at RT to 1.0 x 10@super -7@ Pa H2O revealed that the hydroxyl chain structure was formed at the line vacancy site. After H@sub 2@O exposure, annealing at above 500 K was sufficient to remove the hydroxyl chains on the TiO@sub 2@(110) surface, and then line vacancy structures reappeared on the surface. Before published STM and other experimental results supported that dissociative adsorption of water occurs on oxygen vacancy sites of the TiO@sub 2@(110). Therefore these results concluded that the hydroxyl chain structure was formed at the line vacancy site. Thus the formation of the hydroxyl chain structure suggests that controlling of surface hydroxyl groups on catalysis surfaces is possible.

SS-MoP30 Local Nanodeposition of Oxides with Focused Beams - Improving Material and Interface Quality*, H.D. Wanzenboeck, **M. Fischer**, S. Mueller, J. Gottsbacher, W. Brezna, M. Schramboeck, A. Tomastik, H. Stoerti, H. Hutter, E. Bertagnolli,* Vienna University of Technology, Austria

The fabrication of silicon oxide by direct-write deposition with a focused beam is an advanced nano-engineering technique. This locally confined chemical vapour deposition is a versatile tool for tailored surface modification. Two alternative methods - deposition with a focused ion beam (FIB) and a focused electron beam (FEB) - are compared. A silicon precursor such as siloxane is adsorbed on the surface and decomposed by the energy of the focused electron or ion beam. The chemical and physical phenomena at the oxide surface were investigated experimentally and by simulation of the energy dissipation of the incident beam. The process stage adsorption, surface diffusion, surface reactions, and layer growth are discussed. This work demonstrates the capability of this maskless method to fabricate arbitrary geometries of oxide and to create real 3-dimensional nanostructures. The material qualities of silicon oxide surfaces obtained with both methods are compared by chemical analysis, vibrational spectroscopy, optical and electrical characterisation. The beneficial addition of oxygen is reported and the optimum process window is identified. The chemical composition and the topography of the oxide surface are investigated by Auger electron spectroscopy (AES) and atomic force microscopy (AFM). A correlation between process parameters and the surface properties was found. The interface between the deposited microstructures is investigated by secondary ion mass spectroscopy (SIMS) and by electrical characterisation of capacitor devices with the deposited silicon oxide. Results indicate significant atomic mixing at the interface with FIB induced deposition, while a sharp interface can be obtained with the electron beam. This work contributes to a fundamental understanding of oxide formation on the nanoscale by beam induced deposition. This emerging maskless nanotechnique promises applications in MEMS, optical microstructures and dielectrics for semiconductor devices.

SS-MoP31 Structure and Growth of Small Au Particles on TiO@sub 2@(110)*, **D. Pillay**, G. Hwang,* The University of Texas at Austin

*****PLEASE NOTE: YOU MUST IDENTIFY A DIFFERENT PRESENTER FOR THIS ABSTRACT. YOU MAY PRESENT ONLY ONE (1) PAPER AT THE CONFERENCE*****While Au is known to be chemically inert in its bulk form, nanometer size Au particles dispersed on TiO@sub 2@ have been found to exhibit high activities for a variety of catalytic oxidation processes at or below room temperature. Au atoms weakly interact with the TiO@sub 2@ surface and become unstable toward sintering in response to changes in the gaseous environment even at moderate temperatures. Given the weak Au-TiO@sub 2@ interfacial interaction, Au particle nucleation is thought to predominantly occur at the sites of surface defects, such as (bridging) oxygen vacancies. Similarly, during oxidation processes, a reactant O@sub 2@ molecule may adsorb on the vacancy site molecularly or completely heal the defect (while ejecting an oxygen atom). Oxygen species may also interact with Au particles directly or indirectly. Thus, oxygen adspecies can greatly alter TiO@sub 2@ surface properties and Au-TiO@sub 2@ interfacial interactions, which may in turn influence the nucleation, growth, and sintering of Au particles. In this poster, we will present the results of our recent density functional theory calculations on the interactions between oxygen species and small Au particles on TiO@sub 2@ (110), with a focus on understanding i) the dynamics of oxygen species on Au/TiO@sub 2@ and ii) the effect of oxygen species on Au particle nucleation, growth, and sintering.

SS-MoP32 Gas-Phase Catalytic Processes on Metal-Oxide Supported Gold Nanoparticles*, **B. Roldan Cuenya**,* University of Central Florida

Our experimental work aims to improve the understanding of the processes taking place in nanocluster-catalyzed reactions by systematically studying how the nanoparticle size and shape affects its chemical reactivity. For this purpose, the low temperature carbon monoxide oxidation reaction on metal-oxide-supported gold nanoparticles will be used as a model system. Different ex-situ wet chemistry methods such as nanosphere lithography or the self-assembly of metal loaded block-copolymer micelles are being used to create ordered arrays of size- and shape-selected nanospheres, nanorods and triangular nanoprism catalysts. In addition, in-situ (UHV) nanoparticle size and shape modifications by high temperature annealing, Ar+ sputtering and O2-/H2 plasma treatment are being conducted. Interconnections between directly measurable electronic phenomena and surface chemistry will be established and used to provide insight into catalytic reactions. Temperature-Programmed Desorption (TPD), Atomic Force Microscopy (AFM), Scanning Tunneling Microscopy (STM), and X-ray Photoelectron Spectroscopy (XPS) are being employed to characterize the changes induced in the metal nanoclusters and their supports upon gas exposure. Our approach relies on the combination of ex-situ size- and shape-selected nanoparticle preparation methods and in-situ reactivity characterization measurements at different stages of well-controlled thermally and chemically induced size and shape transformations.

SS-MoP33 The Preparation and Chemical Reaction Kinetics of Microcrystalline Tungsten Bronze Thin Films with Peroxide and Nitrobenzene Solutions*,* ***N.F. Materer****, A. Apblett, E.B. Kadossov, K. Khan, E.F. Shams,* Oklahoma State University

Microcrystalline tungsten bronze (HxWO3) thin films are prepared using wet chemical techniques or atomic hydrogen to reduce a tungsten oxide thin film. The oxide film is prepared by thermal oxidation of sputter deposited tungsten metal film on a quartz substrate. The crystallinity of these films is determined by X-ray diffraction. X-ray and ultra-violet photoelectron spectroscopy show that these films are indistinguishable from conventionally prepared tungsten bronze powders. In addition, platinum or silver metal is deposited on these films. The quartz support allows the total amount of incorporated hydrogen in the film to be quantified by monitoring the absorbance at 900 nm. This technique is utilized to study the oxidation kinetics of these films by either organic nitrides or peroxides. A satisfactory fit to a kinetic model that involves two simultaneous processes is obtained. The first one is the proton diffusion from the bulk of the film to its surface, and the second is a reaction of the surface proton with the oxidant. In the latter process it is assumed that the surface concentration of the oxidant is effectively constant. The proton diffusion coefficient and the activation energy for the reaction of tungsten bronze films with oxygen gas are also estimated. The addition of catalytic amounts of platinum or silver on the rate is also discussed.

Thin Films
Room Exhibit Hall C&D - Session TF-MoP
Aspects of Thin Films Poster Session

TF-MoP2 Effects of Annealing Gas on Characteristics of HfO@sub 2@ Deposited by ALD for MIM Capacitors*,* ***S.-W. Jeong****,* H.J. Lee, *K.-S. Kim, M.-T. Yoo,* Sungkyunkwan University, Korea*; Y.-H. Roh,* Sungkyunkwan University, Korea, Republic of Korea*; T. Noguchi, J. Jung, W. Xianyu,* Samsung Advanced Institute of Technology, Korea

Research on the insulating films in metal-insulator-metal (MIM) capacitors has focused on ways to increase the dielectric constant of insulator to improve the packing density of integrated RF capacitors. High-k oxide (e.g., Ta@sub 2@O@sub 5@) has been suggested as an alternative material to replace SiO@sub 2@ and Si@sub 3@N@sub 4@. However, reliability problem caused by leakage current may limit the application of Ta@sub 2@O@sub 5@. Properties of HfO@sub 2@ grown on the Si substrate shows a dielectric constant which is comparable to that of Ta@sub 2@O@sub 5@. Further, the characteristics of HfO@sub 2@ more stable than those obtained from Ta@sub 2@O@sub 5@, suggesting that we may use HfO@sub 2@ film as insulator in MIM capacitor. In this work, we report the physical and electrical properties of ALD-deposited HfO@sub 2@ film (11-12 nm) annealed at various gases (N@sub 2@, O@sub 2@, N@sub 2@O). HfO@sub 2@ films were annealed at 400, 600, 800 °C using a rapid thermal processor for 1 min. Top and bottom metal electrodes were Pt and Pd, respectively. The electrical characterization indicates that HfO@sub 2@ MIM capacitors fabricated at 800 °C under O@sub 2@ ambient show the most desirable electrical properties, such as a high capacitance density of ~16.9 fF/µm@super 2@, a low leakage current of 2.7*10@super â?"4@ A/cm@super 2@ at -5 V, low-voltage coefficients of capacitance, and good-frequency dispersion properties. In addition, better properties were obtained from the samples annealed using N@sub 2@O than those of samples treated using N@sub 2@. These results indicate that oxygen content has certain role(s) on the electrical properties of ALD-deposited HfO@sub 2@ film. These results, as well as further investigation of physical properties of the samples using XPS, will be presented at the conference.

TF-MoP3 The Annealing Effect on the Diamond-Like Carbon Protective Antireflection Coating*,* ***W.S. Choi****, K. Kim, J. Yi, B. Hong,* Sungkyunkwan University, Korea

Diamond-like carbon (DLC) film has many advantages like diamond film beside it has wide band gaps and its refractive index can be adjusted variably so the film can be utilized as protective coating for IR windows and anti-reflective coating for solar cells. In this study, DLC films were prepared by RF-PECVD (Plasma Enhanced Chemical Vapor Deposition) method on silicon substrates using methane (CH4) and hydrogen (H2) gas. We examined the effects of the post annealing temperature and the annealing ambient on tribological and optical properties of the DLC films. The films were annealed from 300 to 900oC in steps of 200oC by RTA equipment in different ambient. The thickness of the film was observed by a scanning electron microscope (SEM) and surface profiler. The structure and surface morphology of the films were examined using Raman spectroscopy, X-ray diffractometer and atomic force microscopy. The hardness and depth profile of the DLC film were measured with nano-indentor and Auger electron spectroscopy, respectively. The optical properties of DLC thin film were investigated by UV/VIS spectrometer, Fourier transform infrared spectroscopy (FT-IR) and ellipsometry. And also, we have checked their carrier life time.

TF-MoP5 Metalorganic Chemical Vapor Deposition and Characterization of Zr-silicate Gate Dielectrics*, J. Kim,* ***S. Lee****, K. Yong,* POSTECH, Korea

Zirconium silicate [ZrSi@sub x@O@sub y@] film, demonstrating good thermal stability in direct contact with Si, is a very promising candidate to replace SiO@sub 2@ (k=3.9) gate dielectrics. Zr-silicate films were deposited by injecting tetrakis-diethylamido-zirconium [Zr(NEt@sub 2@)@sub 4@] and tetra-n-butyl-orthosilicate [Si(O@super n@Bu)@sub 4@] precursors all together into metal-organic chemical vapor deposition (MOCVD) reactor. The growth rate was about 1 nm/min at 450~500 @super o@C. High-resolution TEM image of Zr-silicate films showed an atomically flat interface of silicate/silicon even in ultra thin films and showed smooth surface with RMS (root mean square) value of 0.5 nm. The Zr/(Zr+Si) ratio was average 0.2 for the bulk film, indicating a Si-rich composition. However at the silicate/silicon interface, it shows a higher Zr concentration than Si, implying a Zr-rich composition at the interface. Zirconium silicate films with ~30 % ZrO@sub 2@ were amorphous up to 800 @super o@C and above 900 @super o@C, phase separation of the films occurred into ZrO@sub 2@ and Zr-silicate phases. Amorphous silicates are desirable in order to avoid dislocations and grain boundaries, which provide pathways for diffusion of dopants from the electrode to the substrate and may exhibit high leakage paths. ZrSi@sub x@O@sub y@ exhibited a leakage current density of 1.6 x 10@super -4@ A/cm@super 2@ at a gate bias of 1 V for an equivalent oxide thickness of 4.3 nm and showed very low hysteresis volatage (delta VFB) below 0.02 V, which indicates the low impurities and defect contents in Zr-silicate films.

TF-MoP6 Isotopically Concentrated Silicon Film Formation by Chemical Vapor Deposition*,* ***H. Yamamoto****,* Japan Atomic Energy Research Institute, Japan*; H. Ohba,* Japan Atomic Energy Research Institute*; M. Sasase,* The Wakasa-wan Energy Research Center, Japan*; K. Yamaguchi, K. Shimura, S. Shamoto, A. Yokoyama, K. Hojou,* Japan Atomic Energy Research Institute

Isotopically concentrated silicon (@super 30@Si) film has been attempted to form by means of chemical vapor deposition. The natural isotope @super 30@Si can be transmuted into stable @super 31@P by the capture of a thermal neutron. If the @super 30@Si enriched layer is formed on the @super 28@Si or natural Si substrate, the enriched layer can act as "donor doping layer" by the transmutation. However, it is hard to obtain plenty of enriched @super 30@Si, since its natural abundance is only 3.1%. Recently, a method for highly efficient enrichment of @super 30@Si in a form of @super 30@SiF@sub 4@ has been established by Yokoyama et al.@footnote 1@ In the present study, the @super 30@Si enriched film (~several tens nm) was deposited on natural Si substrate by using RF plasma (13MHz, 300W) from gaseous mixture of SiF@sub 4@ and H@sub 2@ diluted with Ar. The optimum condition of Si deposition has been investigated by using natural SiF@sub 4@. Obtained film was characterized by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and transmission electron microscopy (TEM). XPS results showed that an impurity phase appeared in the deposited film depending on the H@sub 2@/SiF@sub 4@ gas flow rate ratio and temperature during deposition. For example, the film contained ~10at.% of fluorine in the case of the gas ratio of 2~4 at 250°C. Even though the fluorine content decreased drastically with the increase of the gas ratio up to 10, it still remained at this temperature. The fluorine was not observed in the sample deposited at 400°C. Results of the other analyses will be also presented and discussed. @FootnoteText@ @footnote 1@A.Yokoyama, H.Ohba, et al., Appl.Phys.B 79 (2004) 883-889.

TF-MoP7 SiN Single Passivation Layer Grown by Linear Antenna Type Inductively-Coupled-Plasma Chemical Vapor Deposition for Top-Emitting Organic Light Emitting Diodes*, H.-K. Kim, M.S. Kim, K.-S. Lee, S.H. Jeong, K. Kim,* Samsung SDI

Thin film single passivation layers (SiH@sub x@:H) for top-emitting organic light emitting diodes (TOLEDs) were deposited at substrate temperature of 40°C by using linear antenna type inductively-coupled-plasma chemical vapor deposition (ICP-CVD). It was found that the deposition rates were mainly determined by SiH@sub 4@ flow ratio at low temperature. Even at the low substrate temperature of 40°C, SiN@sub x@:H films showed a good moisture resistance and transparency of 10@super -5@g/m@super 2@/day and 92% respectively. In addition, current-voltage results showed that the SiN@sub x@:H deposition process produced negligible plasma damage, which was generally observed by plasma-related deposition processes.

TF-MoP8 Effect of Hydrogen Dilution on Microstructure of In Situ Polycrystalline Si Film Grown by Catalyzer Enhanced Chemical Vapor Deposition*, **M.S. Kim**, H.-K. Kim,* Samsung SDI

The effect of hydrogen dilution on microstructure of in situ polycrystalline Si (poly-Si) films grown by catalyzer enhanced chemical vapor deposition (CECVD) has been investigated. It was shown that microstructure of the Si films grown at low substrate temperature (<300 °C) in CECVD was strongly affected by hydrogen dilution ratio (H@sub 2@/SiH@sub 4@). In addition, a secondary ion mass spectroscopy (SIMS) depth profile of the in situ poly-Si film grown by CECVD at SiH@sub 4@/H@sub 2@ (1/40 sccm) exhibited much lower hydrogen concentration than dehydrogenated amorphous Si film grown by conventional plasma enhanced chemical deposition (PECVD). These results indicated that the CECVD technique is a promising candidate to grow high quality in situ poly-Si films on glass or flexible substrate for low-temperature poly-Si (LTPS) and flexible displays.

TF-MoP9 Irradiation Effect of Nitrogen Ion Beam on Hydrogenated Amorphous Carbon Films*, **Y. Watanabe**, S. Katoh, N. Kitazawa,* National Defense Academy, Japan

Hydrogenated amorphous carbon (a-C:H) thin films were deposited on silicon single crystal substrates from toluene vapor using rf plasma at room temperature. After deposition, the a-C:H films were irradiated with a nitrogen ion beam and effects of nitrogen ion beam irradiation on surface morphology and composition were studied. Nitrogen ion irradiation was performed using a nitrogen ion beam of 0.2 to 1.5 keV for 10 min under the constant ion current density at room temperature. Surface morphology was observed by atomic force microscopy (AFM). Changes in composition and carbon-nitrogen bonding states were analyzed by X-ray photoelectron spectroscopy (XPS). Carbon structures were examined by Raman spectroscopy. AFM observations revealed that the film surface became smooth after nitrogen ion beam irradiation and notable difference in surface smoothing is hardly observed between 0.2 and 1.5 keV ion irradiation. XPS studies showed that nitrogen was absorbed near the surface of the a-C:H films after nitrogen ion irradiation and combined with carbon, resulting in carbon nitride formation. Depth profiles obtained by XPS showed that 1.5 keV nitrogen ion irradiation is more effective for carbon nitride formation than 0.2 keV ion irradiation. Carbon structures did not change remarkably after nitrogen ion irradiation. These results show that irradiated nitrogen ions are absorbed into the a-C:H films to form carbon nitride layers near the surface. The effect of the nitrogen ion energy on surface morphology and nitrogen implantation will be discussed.

TF-MoP10 Fabrication of Micropatterned Mesoporpous Silica Films on a Flexible Polymer Substrate Through a Pattern Transfer and Subsequent Photocalcination*, **A. Hozumi**, M. Inagaki, Y. Yokogawa, T. Kizuki,* AIST, Japan*; N. Shirahata,* NIMS, Japan

Mesoporous silica (MPS) have attracted much attention due to their advanced applications. In order to fabricate microdevices from such nanoporous materials, they must be formed into microstructured thin films on certain substrates. In particular, such microfabrication on polymeric surfaces has been attracting more and more attention to fabricate flexible microdevices. In this study, we report a novel way to fabricate MPS microstructures on the flexible polymer substrate based on a pattern transfer method. First, fluoroalkylsilane (FAS) self-assembled monolayer (SAM)-covered Si substrate was photolithographically micropatterned. Next, the second SAM, e.g., aminosilane (AEAMPS) SAM was site-selectively formed onto lithographically defined patterns through a liquid phase process. The substrate was then immersed in a solution consisting of tetraethoxysilane, cetyltrimethylammonium chroride, hydrochloric acid and water. As evidenced by AFM, surfactant-silica composite film was preferentially deposited on the FAS-SAM regions, while undesirable deposition was not observed on the AEAMPS-SAM regions. In order to transfer the micropatterns to the polymer substrate, they were attached firmly to the polymer surface. Subsequently, the polymer substrate was heated to its glass transition point and was kept at this temperature for 1 hour under the pressure of 2~4 MPa. AFM, EDS and XRD confirmed that the micropatterns were successfully transfered to the polymer substrate without distortion their morphologies and nanostructures, since the adhesion of the micropatterns and the FAS-SAM surface was very weak. Finally, on the basis of photocalcinationt, the micropatterns were exposed to172 nm vacuum UV light for 3 hours at 10 Pa to eliminate surfactant molecules in order to obtain nanopores. The resulting MPS micropatterns adhered very tightly to the polymer substrate and never peeled off even after a tape peeling test.

TF-MoP11 XPS and FTIR Characterization of C60 States in C60 Doped Conducting Polymers*, **H. Kato**, S. Takemura, K. Iwasaki, N. Nanba, T. Hiramatsu,* Kanto Gakuin University, Japan*; O. Nishikawa, M. Taniguchi,* Kanazawa Institute of Technology, Japan

Conducting polymer polythiophene (PT) film incorporated with C60, highly functional molecule, was prepared by electrochemical doping and diffuse injection methods. Charge transfer and interaction between the doped dye molecule and PT polymer chains were investigated by XPS analysis of the core-level energies and spectral profiles of the atomic components. Vibration states of the doped dye molecule and the polymer backbone were also investigated by FTIR RAS and FTIR transmission in order to examine the dopant-chain interaction in the hybrid films. The XPS spectral profile of the electrochemical doping sample was different from that of the casting sample, which reflects the different dopant-chain interaction in polymer films. It is known that C60 is a highly symmetrical molecule with HOMO fivefold (hu) and LUMO threefold (t1u) enables various valence values to be possible filling the degenerate LUMO levels with different number of electrons. The higher binding energy peaks of C 1s reflect the valence values of C60. FTIR transmission measurement clarified that C60 molecules were doped in the polymer film by both methods of electrochemical doping and casting because characteristic peaks due to the vibrational modes of C60 were observed. The C60 originated peaks were also observed in the FTIR RAS spectra. The peaks due to C60 were differently observed in the spectra of electrochemical doping and casting samples reflects the different doping states of C60. The results of XPS and FTIR suggests the controllability of conductive state of PT by changing dopant valence values by electrochemical doping methods. XPS core-level analysis of S 2p was composed of several peak components. The energy position of the main peak is almost positioned in the reference value. The lower energy and the higher energy components reflect the charge transfer between polymer chain and C60 molecule. The present work supported by "High-Tech Research Center" Project aided by MEXT.

TF-MoP12 XPS Characterization of Electrochemical Growth of Conducting Polymer on Oxidized Si Surface*, H. Kato, **S. Takemura**, N. Takakuwa, K. Ninomiya, T. Watanabe, N. Nanba, T. Hiramatsu,* Kanto Gakuin University, Japan

Electrochemical growth of conducting polymer polythiophene (PT) film on oxidized Si wafer was closely investigated by XPS. Initial stage of polymer growth was investigated by analyzing the core-level energies and spectral profiles of the atomic components. Oxidized Si surface was also closely characterized by XPS by using curve-fitting of Si 2p and Si 2s core-level spectra to determine precisely the Si covalent states of surface layers. The purpose of the present work is to clarify the interface between an organic upperlayer and oxidized Si sublayer which is an interesting issue from practical point of view in wet fabrication techniques. The XPS spectrum of Si 2p and Si 2s of the oxidized substrate surface was composed by 5 peaks which correspond with Si valence values, such as Si, Si+, Si2+, Si3+, SiO2. The core-level energy positions of those different states were determined by XPS. The Si wafer was prepared through several stages of cleaning process. The surface roughness was reduced and the STM image of nano-scale orederd surface was obtained although the surface layers were oxidized investigated by FTIR RAS and XPS measurements. Electrochemical PT growth at initial stage was implemented on the oxidized Si substrate. Obtained XPS spectra of Si 2p and 2s showed that the Si+ peak grew associated with polymer deposition. This experimental fact reflects the interface linkage between organic polymer chain and Si oxidized layer. The bonding between organic and inorganic species will be also discussed. The present work supported by "High-Tech Research Center"Project aided by MEXT.

TF-MoP13 Controlled Synthesis and Magnetic Properties of Iron Oxide Particles Formed by Thermal Decomposition of Rapidly Expanded Supercritical Solutions*, S. De Dea, D. Graziani,* ***D.R. Miller****, R.E. Continetti,* University of California, San Diego

Films of iron oxide fine magnetic particles were synthesized by rapidly expanding a supercritical solution (RESS) of ferric acetylacetonate (FeAA) and CO@sub 2@ onto a hot silicon wafer. The temperature of the substrate was set at a value such that thermal decomposition of the solute would occur at the silicon surface with subsequent formation of iron oxide particles in an oxidizing atmosphere. We present the details of the RESS apparatus and initial data on the FeAA/CO@sub 2@ system and the deposited thin films. In the RESS process particle morphology and composition can be controlled by adjusting process parameters such as pre-expansion temperature, pressure and composition of initial solution, temperature of the substrate, nozzle to substrate distance, and expansion chamber pressure and composition. In the process design and utilization of RESS it is very important to acquire accurate solubility data and then to monitor the composition of the expanding solution. For this purpose a spectroscopic view cell was introduced in the RESS system, prior to the expansion, to allow both equilibrium solubility as well as on-line concentration measurements. Obtained solubility data will be presented and compared with predicted solubility from the Peng-Robinson equation of state. The deposited particles were analyzed with SEM, XRD, EDX and a SQUID based magnetometer. It was found that smaller nanoparticles were formed when the RESS expansion was into the vacuum. The effect of the supersonic expansion jet structure on particle morphology will be discussed. EDX and XRD showed that complete decomposition of FeAA occurred at the silicon surface and that the particles consisted of a mixture of crystalline Fe@sub 2@O@sub3@ and Fe@sub 3@O@sub 4@. Magnetization measurements were performed at different temperatures and they showed that the particles have ferromagnetic properties. Results for the coercive field as well as saturated and remanent magnetization will be presented.

TF-MoP14 Growth of Novel NaCdF@sub3@ Thin Films by Pulsed Laser Deposition for Advanced Ferroelectric Applications*,* ***T. Aburada****, C.T. Nelson,* University of Virginia*; R.W. Smith,* University of Nebraska-Omaha*; S.B. Qadri,* US Naval Research Laboratory*; J.M. Fitz-Gerald,* University of Virginia

Ferroelectrics are an important class of materials in a variety of applications including, non-volatile random access memories.@footnote 1@ Recent computer simulations have predicted that NaCdF@sub 3@ has a ferroelectric ground state.@footnote 2@ Moreover, NaCdF@sub 3@ is predicted to have a large energy band gap and be transparent in the UV spectrum, thus having potential for use in electro-optic applications.@footnote 2@ Thin films of NaCdF@sub 3@ were grown by Pulsed Laser Deposition (PLD) on Si (100) substrates using a high purity NaF and CdF@sub 2@, 1:1 molar fraction, starting target in a high vacuum chamber. A KrF excimer laser (@lambda@ = 248 nm) was used to deposit films as a function of growth temperature, system pressure, and laser energy. All films exhibited a large degree of roughness along with pronounced surface irregularities, as evidenced by Scanning Electron Microscopy (SEM) images. X-ray Diffraction (XRD) data showed that the films consist of two binary phases: CdF@sub 2@ and NaF, closely matching the stoichimetries of the starting target constituents. Although XRD analysis indicates the absence of the ternary NaCdF@sub 3@ phase, it is important to point out that oxide peaks are not observed. This is a significant hurdle to overcome in producing these materials. Compositional measurements by Energy Dispersive X-ray Spectroscopy (EDXS) indicate that the atomic fraction of Na to Cd is lower in the deposited thin film than in the initial target material. A comparison of the XRD spectra of the deposited film and the target reveals a decrease in the NaF phase in the films. With the large band gap associated with NaF, KrF irradiation is not the optimum choice due to its relatively low energy of 5eV. @FootnoteText@ @footnote 1@J.S. Horwitz, K.S. Grabowski, D.B. Chrisey, R.E. Leuchtner, Appl. Phys. Lett. 59 (13), 23 (1991)@footnote 2@ C. Duan, W.N. Mei, J. Liu, W. Yin, J. R. Hardy, R.W. Smith, M.J. Mehl, L.L. Boyer, Phys. Rev. B 69, 033102 (2004).

TF-MoP15 Low Temperature Formation of High-Quality SiO@sub 2@ Thin Film using UV Light-Excited Ozone*,* ***A. Tosaka,*** National Institute of Advanced Industrial Science and Technology, Japan*; T. Nishiguchi,* Meidensha Corporation, Japan*; H. Nonaka, S. Ichimura,* National Institute of Advanced Industrial Science and Technology, Japan

Fabrication of high quality SiO@sub 2@ film at low temperature is required for a gate dielectric film in thin film transistor for future display devices. We have developed an oxidation system using highly concentrated ozone excited by KrF laser light (248 nm) since it is expected that ozone molecules exposed to 248 nm light readily decompose into excited oxygen atoms, O(@super 1@D), and oxygen molecules. It was revealed that the UV excited ozone results in SiO2 film growth more than 3.6 nm thickness at 70 °C within 10 min., sufficiently thick as a barrier oxide. The growth rate behavior shows that there are two oxidation mechanisms and the activation energy is almost zero (0 to 5 min.) and 0.14 eV (after 5 min.), respectively. The low activation energy is due to the reaction between highly-reactive O(@super 1@D) and the silicon surface layers whose electric state is UV-excited. The current density (J)-electrostatic field (E) characteristics of the SiO@sub 2@ film show the ideal tunneling current properties, indicating that the KrF laser light irradiation does not induce defects in the film. Details reaction mechanism of O(@super 1@D) with silicon in terms of the density of excited oxygen atoms will be also discussed.

TF-MoP16 Influences of the Dopant Concentration and Thermal Treatment on Optical and Electrical Properties of C-oriented Aluminum-Doped Zinc Oxide Films*, S.-Y. Kuo,* National Applied Research Laboratories, Taiwan*;* ***W.-C. Chen,*** National Taiwan Normal University, Taiwan*; C.Y. Su,* National Applied Research Laboratories, Taiwan*; C.-P. Cheng,* National Taiwan Normal University, Taiwan

Transparent and conductive Al-doped zinc oxide (ZnO:Al, AZO) thin films with highly preferential c-axis orientation have been prepared by the sol-gel technique. Structural, electrical and optical properties were performed by XRD, AFM, SEM, four-point probe, photoluminescence (PL) and UV-VIS transmission measurements. The influence of dopant concentration and thermal treatment on the microstructure as well as on the electrical and optical properties of the thin films is investigated. It was found that the FWHM of XRD patterns reach a minimum at annealing temperature of 750 @super o@C, which is consistent with the results of SEM images. Room-temperature PL spectra show two main peaks centered at about 380 nm (UV) and 520 nm (green). The variation of UV-to-green band emission was greatly influenced by annealing temperatures. The minimum sheet resistance of 10@super 5@ @ohm@/sq. was obtained for the film doped with 2 wt.% Al, annealed at 650 @super o@C. Meanwhile, all AZO films are very transparent, between 85 and 95 % transmittance, within the visible wavelength region. The optical absorption edge was found to blueshift with increasing doping concentration as well. Possible causes to the above will be given and discussed. These results indicate that AZO thin films might be a promising candidate for future photonic applications.

TF-MoP18 Electrical, Optical and Structural Properties of Arsenic-doped (Zn,Mg)O Films*,* ***J.-M. Erie****, Y.J. Li, H. Kim, K Ip, S.J. Pearton, V. Cracium, D.P. Norton, J. Chen, F. Ren, I. Kravchenko,* University of Florida

Zinc oxide is an attractive compound semiconductor for transparent electronics, UV light emitting diodes (LEDs) and laser diodes (LDs). It possesses a direct band gap of 3.37eV, a large exciton binding energy of 60 meV and a high theoretical saturation velocity. However, the formation of p-type material with a high hole carrier density remains a major challenge. Recent efforts have focused on ZnO p-type doping with group V anions, namely N, P or As. In this work, the synthesis and properties of As-doped (Zn,Mg)O thin films grown by pulsed laser deposition are reported. Epitaxial (Zn,Mg)O films doped with 0.02-0.2 at % As are grown using a single ablation target synthesized with high-purity zinc arsenide as the source of arsenic. The structure and phase formation are characterized as a function of growth temperature and oxidation conditions. Both oxygen and ozone are explored as oxygen source gases. Film properties are characterized using Hall measurement, photoluminescence, scanning electron microscope, and X-ray diffraction. This work was supported by the National Science Foundation, Air Force Office of Scientific Research, the Department of Energy, and the Army Research Office. The authors would also like to acknowledge the Major Analytical Instrumentation Center, Dept. of Materials Science and Engineering, University of Florida.

TF-MoP19 Fe(001) Thin Films for Novel Applications*,* ***C.A. Meserole****, G.L. Fisher, D.J. Hilton, R.D. Averitt, D.J. Funk, A.J. Taylor,* Los Alamos National Laboratory

The electrical and magnetic properties of thin iron (Fe) films have sparked significant scientific interest. Our interests are two-fold. First, Fe(001) films are ideal targets for a newly developed ultrafast x-ray diffraction instrument designed to understand complex behavior, such as melting or solid-solid phase transitions, in shock-loaded materials. The instrument utilizes an intense laser pulse to initiate a shock wave in the sample and x-ray diffraction to study the material's response. This target/instrument combination will allow for directly comparing experimental data to published molecular dynamics simulations of a shock wave propagating along the [001] direction in an Fe crystal. Second, we have discovered a novel application for thin Fe films, which generate picosecond, broadband terahertz frequencies after intense femtosecond pulse excitation by a Titanium:Sapphire laser. The terahertz emission provides a direct measure of the induced ultrafast magnetization change. Film thickness not withstanding, the criteria for samples used in both experiments are identical due to the similarities of the experiments. For example, the substrate must permit the epitaxial growth of continuous single/monocrystalline films, yet must be transparent to a pump laser. Fe(001) films grown on MgO(001) substrates make ideal samples for both experiments. Issues such as generating a specific crystallographic orientation in the Fe film, film growth mode, substrate preparation and surface contamination, are discussed, along with an overview of the applications for these films.

TF-MoP20 Electron Cyclotron Resonance Remote Plasma Enhanced Atomic Layer Deposition of Ruthenium Thin Films*, E.-J. Lee, B.-Y. Kim, S.K. Park, H.-D. Kim, J.-W. Park,* ***M.-G. Ko,*** Hanyang University, South Korea

As the silicon process migrates to small device geometries, new deposition process technology will be required to solve the problems obtained with high trench capacitor and ultra thin gate oxide. Attempts to deposit material with atomic level control, atomic layer deposition as a technique which can be available good film uniformity and excellent step coverage have been reported. Ruthenium is a noble metal has low electrical resistivity, high chemical inertness, thermal stability and hardness. Especially, ALD of ruthenium thin films using the metal electrode for trench DRAM capacitor have been researched because the films have not only excellent uniformity also high work function energy of deposited films. In this study, ruthenium thin films prepared by high density plasma ALD with Ru(EtCp)@sub2@ as ruthenium precursor and NH@sub3@ gas as plasma ion source from room temperature to 400°C. ECR remote plasma as high density plasma ion source has over 10@super12@ /cm @super3@ ion density, therefore, ligands of precursor gas can be removed easily. Ruthenium thin films was grown to self-limited reaction process to be ranged from 250°C to 290°C deposited by conventional ALD on 44 nm thick TiN/ 4 nm thick Ti / 100 nm thick SiO@sub2@ / p-type (100) Si wafer. This result reveals that ALD process depends on chemical limited reaction with surface atom and precursor gas, furthermore, this temperature region possess sufficient energy to adsorb ruthenium precursor gas on substrate. Conventional ALD of ruthenium thin film deposited with oxygen and argon mixed gas as a reaction gas is formed ruthenium and ruthenium oxide, however, high-density remote plasma enhanced ALD of ruthenium deposited using NH@sub3@ as a plasma gas is formed only ruthenium films by low angle HRXRD (High Resolution X-ray Diffraction) peaks. Ruthenium thin films deposited by HDPALD have surface morphology of 10 ~ 12 Å, and electrical resistivity of 11 ~ 15 µm cm.

TF-MoP22 Experimental AES and Computer Model Based Elemental Depth-Profile Analysis of Tungsten Carbide Doped Diamond Like Carbon Films*,* ***J.A. Carlson****, J. Abou-Hanna, J. Lozano,* Bradley University

Tungsten-doped diamond-like carbon (DLC) coatings, with a thickness of approximately three microns, have been magnetron sputtered onto 52100 steel with chromium and chromium/tungsten carbide dual interlayers using a Hauzer Techno Coating HTC 1200 4 UBM system. The process gas for the deposition is acetylene. The deposition chamber uses a two degree of freedom rotational system to rotate parts to be coated so that eventually each portion of the part will experience the full impact of the target. Depending on the speed of the rotation, the rotation pattern may take several minutes to repeat. At certain intervals during deposition, the acetylene flow is linearly altered to change characteristics throughout the film. AES sputter depth profiling analysis shows a spatial dependency on the depth profile which is likely attributable to the fixture rotational system. AES depth profiling also reveals trace amounts of titanium within the DLC and within the interlayers. The presence of titanium has further been confirmed with EDS/SEM analysis. Furthermore, AES shows significant amounts of oxygen in the area of the interlayer/substrate interface. Lastly, in addition to the experimental data, mathematical models are presented that were used to predict film chemistry, film thickness, and film structure.

TF-MoP23 Improvement of Surface Roughness in Indium Tin Oxide (ITO) Anode for Organic Light-Emitting Diode (OLED) by Water Vapor Injected Radio Frequency Sputtering*,* ***K.-S. Lee****, D.-G. Kim, H.-K. Kim,* Samsung SDI

We report on improvement of surface roughness in indium tin oxide (ITO) anode which was grown by water vapor injected rf sputtering method, for use in organic light-emitting diode (OLEDs). It is shown that ITO films prepared by water vapor injected rf sputtering have very smooth surface (Rms 20.Å, PtV 174Å), low resistivity (0.00019 Ω/square), and high transmittance (~ 96%). Scanning electron microscopy (SEM), atomic force microscopy (AFM), and x-ray diffraction (XRD) examination results show that film surfaces of ITO were mainly influenced by the preferred orientations in ITO anode films. In addition, secondary ion mass spectroscopy (SIMS) result clearly shows that OH content in ITO film was increased by water vapor injection. OLED with ITO cathode prepared by water vapor rf sputter method show lower turn on voltage as compared to that of OLED with ITO films prepared by rf sputtering without water vapor. Based on SEM, AFM, and XRD results, we describe a possible mechanism to explain improved electrical and surface properties of ITO films prepared by water vapor injected rf sputtering.

TF-MoP24 Characteristics of Indium Zinc Oxide Top Cathode Layer Prepared by Box Cathode Sputtering for Top-Emitting Organic Light-Emitting Diodes*, H.-K. Kim,* ***D.-G. Kim****, K.-S. Lee,* Samsung SDI

We report on plasma damage-free deposition of indium zinc oxide (IZO) cathode layers for top-emitting organic light-emitting diodes (TOLEDs) by using a box cathode sputtering (BCS) technique. A sheet resistance of 42.6W/Â£ and average transmittance above 88% in visible range were obtained even in IZO layers deposited by the BCS at room temperature. The TOLED with IZO top cathode layer grown by the BCS shows electrical characteristics comparable to TOLED with only thermally evaporated Mg-Ag cathode. In particular, it is shown that the TOLED with the IZO top cathode layer deposited by the BCS has very low leakage current density of 1X10@super -5@mA/cm@super 2@ at reverse bias of -6V. This suggested that there is no plasma damage caused by the bombardment of energetic particles during IZO sputtering process. Based on current-voltage, x-ray diffraction (XRD), high-resolution electron microscopy (HREM), scanning electron microscopy (SEM), and atomic force microscopy (AFM) examination results, possible mechanisms to explain plasma damage-free sputtering of the BCS system are suggested.

TF-MoP26 Fabrication of Long Lengths of Flexible High Temperature Superconductor Thin Film Tapes for Electric Power Applications*,* ***V. Selvamanickam****, Y. Chen, X. Xiong, Y. Li, Y. Xie, Y. Qiao, J. Reeves, P. Hou, M. Gardner, T. Salagaj, K. Lenseth,* SuperPower

High Temperature Superconductors (HTS) have immense potential in electric power applications such as cables, motors, generators, and transformers. The zero-resistance property of HTS can be beneficially used to transmit up to 10 times more power in cables, and reduce the size and weight of rotating machinery and transformers by half. SuperPower is scaling up the so-called second-generation HTS conductors which are based on thin film tapes of epitaxially grown superconducting films. Flexible metal substrates such as Hastelloy are used and highly biaxially-textured oxide buffer templates are deposited by ion beam assisted deposition and magnetron sputtering. The buffer layers are comprised of a multilayer stack of oxides, each layer comprising of about 10 to 100 nm. Y-Ba-Cu-O superconducting films are then deposited on the buffer stack in thickness of 1 to few microns by metal organic chemical vapor deposition (MOCVD). Overlayers of silver and copper films are used to complete the conductor. SuperPower has established Pilot-scale facilities for producing long lengths of high-performance second-generation HTS thin film tape conductors. We have scaled up the processes to 100 m lengths with critical currents exceeding 100 A at 77 K. In this presentation, we will discuss the recent advances in scale up several thin film process technologies, associated equipment and process control techniques to fabricate second-generation HTS thin film tapes for electric power applications. Prototype electric power devices fabricated with these HTS thin film conductors will also be presented.

TF-MoP27 Flexible Gas Barrier Coatings Based on Roll-to-Roll Symmetric Magnetron Sputtering*,* ***C.-S. Wang****, K. Sasaki,* Kanazawa University, Japan*; S.-F. Chen,* National Taipei University of Technology, Taiwan*; T. Hata,* Japan Science and Technology Agency

Superior gas and water vapor barrier coatings on polyethylene terephthalate substrate were prepared by roll to roll symmetric magnetron sputter technique. It has considerable attention that electronic devices such as flat panel displays, electronic paper and solar cell are to be flexible. In general, replacing the substrate from glass to plastic film, the gas permeability is so high that the oxygen and water vapor through the film damage the device. In this work, a new roll-to-roll coater for 300 mm web width combined with asymmetric magnetron sputtering has been developed to produce flexible gas barrier coating with high productivity.

Three pairs of symmetric magnetron sputtering cathodes were sited on the both side of the substrate to realize subsequent coating of different layers and low-temperature deposition. On the other hand, the gas barrier coatings composed of 4 layered silicon oxynitride and oxide anti-reflection coatings have been investigated to improve resistance of the oxygen and moisture permeability. As experiments, the gas barrier properties were strongly depended on the film density and thickness and indicated that the gas barrier properties of 4 layered coatings were superior to single layer. The results show the transmission rate of water vapor bellow 0.07 cc/m@super 2@-day-atm and the oxygen transmission rates as low as 0.2 cc/m@super 2@-day-atm, moreover, an average transmittance rate of 98% in the range of visible spectrum has been measured. These competitive values of the coating can be actualized a high throughput of up to 1 m/min at economic coating cost.

TF-MoP28 Sputtering of Y3Al5O12:Cr Thin Films for Temperature Sensor Applications*, **Y. Deng**, P.D. Rack,* University of Tennessee

Phosphor materials can be used as a temperature sensor by monitoring the phosphor decay time. Chromium-doped yttrium aluminum garnet (Y3Al5O12:Cr, or YAG:Cr) powders have been used in phosphor thermometry as its decay time has been well calibrated from room temperature to 600 Celsius. While powder paints are useful in some applications, these paints can flake and peel under some harsher environments. To ameliorate this problem, we are exploring the properties of YAG:Cr thin films. In this work, YAG:Cr thin films were sputter deposited in a combinatorial fashion to rapidly determine the optimum chromium concentration. The photoluminescence (PL) properties were correlated to the chromium concentration and an optimum concentration of 0.7 atomic percent was determined. Subsequently, a design of experiments was conducted to study the effects that the substrate temperature, substrate bias, and oxygen flow rate have on the YAG:Cr thin film PL and crystallinity. An optimum sputtering condition was found. Finally, temperature dependent PL intensity was measured as a function of temperature to understand the thermal quenching phenomenon.

TF-MoP29 Film Properties of Transparent Conductive Oxide Films Deposited from Either ZnO- In@sub2@O@sub 3@or ZnO-SnO@sub2@ Systems with Additional Ga@sub2@O@sub3@ Impurities*, **K. Tominaga**, D. Takada, Y. Sukeda, Y. Nishimura, T. Moriga, I. Nakabayashi,* Tokushima University, Japan

Recently transparent conductive oxide films with smooth surface are expected. Lower deposition temperature is also expected for the TCO in polycarbonate substrate. For these applications, amorphous transparent conductive films are expected to be one of adequate materials. Amorphous films can be deposited in the system of ZnO-In@sub 2@O@sub 3@, or ZnO-SnO@sub 2@. Therefore we deposited those films, and investigated the influence of the incorporation of Ga@sub 2@O@sub 3@ on the film properties for those systems. Transparent conductive oxide films deposited from either ZnO-In@sub 2@O@sub 3@ or ZnO-SnO@sub2@ systems with additional Ga@sub2@O@sub3@ impurities were deposited by facing target sputtering system. ZnO:Ga and In@sub2@O@sub3@ targets were used for ZnO-In @sub2@O@sub 3@ films, and ZnO:Ga and In@sub2@O@sub3@ for ZnO-SnO@sub 2@ films. Two targets were sputtered simultaneously in Ar gas at 1 mTorr, and electric current ratio @deruta@=I@sub Zn@/(I@sub Zn@+I@sub In@) or I@sub Zn@/(I@sub Zn@+I@sub Sn@) was adopted as a deposition parameter to change film composition. Discharge current of each target was changed from 0 to 80 mA in order to change the content ratio of Zn/(In+Zn) or Zn/(Sn +Zn) in the film. Compositional ratios in films were estimated by X-ray fluorescence analysis. We could deposit ZnO-In@sub 2@O@sub 3@ amorphous films between Zn/(Zn+In)=0.2-0.5 even at a temperature of 250 Â°C. Low resistivity of the order of 10@super -4@@ohm@cm was attained in amorphous phase. Optical transparency was good for all films. For the amorphous films, optical bandgap energy shifted to higher energy side with decreasing the resistivity. Homologous films were deposited between Zn/(Zn+In)=0.5-0.75. These films had higher resistivity and larger optical bandgap than those of amorphous films. Similar results were obtained for SnO@sub 2@:Sb and ZnO:Ga, although the film resistivities were higher than ZnO-In @sub2@O@sub 3@.

TF-MoP31 Palladium Oxide Composite Films Containing Palladium Metal Phase Fabricated by Reactive Ion Beam Sputter-Deposition*, **T. Ichinohe**, S. Masaki,* Tokyo National College of Technology, Japan*; K. Kawasaki,* TDY Co., Ltd., Japan

Palladium oxide (PdO) is known to be p-type semiconductor with 1.5-2.2 eV band gap, and generally formed by thermal oxidation over 400@super o@C. This study reports the relation between formation of PdO and the parameters of reactive ion beam sputter-deposition, such as various substrate temperatures, deposition rates, and oxygen flow rates. According to X-ray diffraction (XRD) study, PdO(002) mixed with Pd(100) was formed in the films at low substrate temperature (T@sub sub@). When T@sub sub@ was 200@super o@C, the XRD intensity of PdO(002) seemed to become higher than Pd(100), in other words, it was tended to show the ratio of their peak intensities (I@sub PdO@/I@sub Pd@) higher than 1 indicating that the formation of PdO was relatively dominant than that of Pd at T@sub sub@=200@super o@C. The intensity of PdO(002) decreased or sometime disappeared when the films were formed at T@sub sub@=400@super o@C. The optimal parameters of reactive ion beam sputter-deposition can lead to form palladium oxide films at low temperature.

TF-MoP32 Growth and Properties of CdTeO@sub x@ Films by Reactive rf Magnetron Sputtering: CdTeO@sub 3@ a High-quality Transparent Material for Solar Cell Applications*, S. Jiménez-Sandoval,* Centro de Investigación y de Estudios Avanzados del IPN, Mexico*; **J. Carmona-Rodríguez**, R. Lozada-Morales,* Benemérita Universidad Autónoma de Puebla, Mexico*; O. Jiménez-Sandoval, M. Meléndez-Lira, C.I. Zúniga-Romero,* Centro de Investigación y de Estudios Avanzados del IPN, Mexico

CdS/CdTe heterostrtuctures is one of the leading solar cell technologies nowadays. One of the current approaches is the use of thin (~ 100 nm thick) CdS layers to improve cell efficiency. However, as the thickness of the CdS layer is reduced there is a greater chance for the appearance of micro junctions between the p-type CdTe layer and the transparent conducting oxide used as front contact, reducing cell efficiencies. It has been recently suggested that the use of a highly resistive buffer layer could avoid micro shunt formation. In order to gain further insight on the formation of transparent CdTe-based materials, we report on the properties of CdTeO@sub x@ films grown by reactive rf sputtering and of films annealed after deposition. The films were grown under an argon flow of 12 sccm and using oxygen flows of 0, 3, 5, 7, 8, 9, 9.5, 10, 10.5 and 11 sccm. This range of oxygen flows was equivalent to oxygen partial pressures within the chamber from 6.7 x 10@super -5@ (3 sccm) to 1.1x10@super -4@ Torr (11 sccm). The substrate temperature was maintained at 400°C for all growths with deposition times of 35 minutes at 35 W of power applied to the 99.999% pure CdTe target. The X-ray diffraction results indicate that the structure of the films was a mixture of cubic/hexagonal phases, typical of CdTe films, for films grown with oxygen flows of up to 10.5 sccm. This structure, however, is no longer sustained when the oxygen flow reaches 11 sccm. At this point, the X-ray diffraction peaks narrow because the material reaches the stoichioimetry and structure of high-quality CdTeO@sub 3@. Accordingly, the bandgap increases from 1.50 to 1.67 eV as the oxygen flow increases from 3 to 10.5 sccm, and at 11 sccm the band gap jumps to 3.73 eV, becoming a transparent, highly resistive film. Annealing the films for two hours under an inert atmosphere at 450°C does not produce significant changes in the crystalline structure, optical properties or bandgap values.

TF-MoP34 Electron Beam Induced Processing of Nanoscale Features: Process Parameters, Simulated Growth, and Nanoscale Applications*, **P.D. Rack**,* University of Tennessee*; J.D. Fowlkes,* University of Tennessee, US*; S.J. Randolph,* University of Tennessee

The rapid and precise direct write growth of nanoscale features by electron beam induced deposition (EBID) requires the optimization of growth velocity while maintaining nanoscale feature dimensions. There is a vast and complex EBID parameter space includes the precursor gas pressure, the primary electron beam energy, the electron beam current, surface diffusion rates of adsorbed precursor species, thermal effects on desorption, and the cascade of electron species produced by inelastic scattering processes. These variables affect the probability of precursor dissociation and hence determine the feature growth velocity and the size of the structure through a series of complex, coupled nonlinear interactions. A dynamic computer simulation based on Monte Carlo calculation sequences was created to aide in the interpretation of experimental observations by simulating experimental growth conditions. In this presentation, we will describe the parameter space and illustrate some of the complex interactions and introduce a Monte Carlo growth simulation. Experimental observations will be correlated to the simulated results. Finally, several nanoscale devices grown with electron beam induced processing will be demonstrated.

TF-MoP35 Influence of Sputtering target Structure on the Deposited Film Properties*, C.F. Lo,* Praxair Surface Technologies - MRC

This study correlated sputtering targets and deposited film properties in physical vapor deposition (PVD). When the sputtering targets consist of multiple elements, in addition to sputtering parameters, distribution of the individual elements or the constitutional target structure will affect the deposited film properties. In this report, we investigated the influences of target structures, including inter-diffusion between W and Ti in W-10 wt% Ti, precipitate size of Si in Al-1 wt% Si and distribution of Al10Mo inter-metallic phase in Al-2 at% Mo, on the deposited film properties. The results indicated that the greater extent of inter-diffusion between W and Ti of the W-10 wt% Ti target, the higher the compressive stress of the deposited film. The larger the Si precipitates in the Al-1 wt% Si target, the larger the Si precipitates in the deposited film. The larger the Al10Mo inter-metallic phases in the Al- 2 at% Mo, the less but larger whiskers generated on the annealed films. These evidences suggest that, although the films are formed by re-arrangement of the bombarded atoms from the sputtered target, mirror effect from target to film exists via PVD.

TF-MoP36 Reactive Pulsed DC Magnetron Sputtering of Oxide Films*, M. Ye,* Applied Materials, Inc.

Reactive pulsed DC magnetron sputtering extends the capabilities of DC sputtering to the area of insulating thin films deposition. The occurrence of arcing can be avoided and the plasma can be stabilized by periodically discharging the poisoned regions of the target through target voltage reversals. By careful design of hardware and selection of appropriate operating conditions, successful processing of various oxide films (aluminum oxide, tantalum oxide, and titanium oxide, etc.) on Applied Materials 200mm Endura platform is demonstrated in this paper. The experimentally established hysteresis curves are compared with modeling analysis. Film characterization results, including deposition rate, film stress, composition, optical index of refraction, density, and roughness, are presented. The effects of oxygen flow rate are studied. It is shown that amorphous films with low stress level, good adhesion, smooth surface and the right stoichiometry can be achieved. Oxide films have been used in a variety of applications, including semiconductor devices, optical films, and MEMS devices. Compared to other deposition methods, DC magnetron reactive sputtering proves to be a simple yet powerful and efficient way of depositing insulating thin films, in both manufacturing environment and R&D applications.

TF-MoP37 Synthesis and Characterization of SiN@sub x@ Films Deposited on Silicon by Reactive RF Sputtering@super *@*, C. Mendoza-Barrera*, *E. Valaguez,* UPIITA-IPN, México*; A. Garcia-Sotelo, V. Altuzar, M. Melendez-Lira, A. Mendoza-Galván,* Cinvestav-IPN, México*; S. Jiménez-Sandoval,* Cinvestav-IPN, México, Mexico

Silicon nitride SiN@sub x@ is a widely used compound in the area of sensors because its electric an optoelectronic properties when it is grew at temperatures lower than 400°C. Also it is employed as buffer layer to deposit films of metallic nanoparticles which are employed as seed for nanotubes grown. We report details of the deposition of SiN@sub x@ thin films by reactive R.F. sputtering on silicon along with results of their structural and optical characterization. The effect of substrate temperature and power intensity of the radiofrequency on films properties were evaluated. Radiofrequency power intensities between 100 and 300 W and substrate temperatures between 100 and 300 °C were studied. Structural and optical characterization were carried out by X-ray diffraction, energy dispersive of X-ray spectroscopy, atomic force microscopy and UV-Vis, Raman and ellipsometry spectroscopies. As expected results indicated that SiNx was produced with optical and structural properties depending on growth parameters. Results are discussed taking in account the stoichiometry obtained under the different growth conditions and the possibility of a porous structure of SiN@sub x@. @FootnoteText@ *Work partially funded by CONACyT-Mexico.

TF-MoP38 Optical and Charge Transport Properties of p-type (CdTe)@sub x@Cu@sub y@O@sub z@ Films: a Novel Material for Photovoltaics and other Optoelectronic Applications*, S. Jiménez-Sandoval,* Cinvestav-IPN, Mexico*; J. Carmona-Rodríguez,* Benemérita Univerisidad Autónoma de Puebla, Mexico*; O. Jiménez-Sandoval,* Cinvestav-IPN, Mexico*; R. Lozada-Morales,* Benemérita Universidad Autónoma de Puebla, Mexico*; M. Meléndez-Lira, C.I. Zúniga-Romero,* Cinvestav-IPN, Mexico

Cadmium Telluride is a technologically important semiconductor material for optoelectronic applications; more specifically, for photovoltaic applications and infrared detection. The search for CdTe-based materials that may improve some of the still difficult matters regarding CdTe-based technology is currently underway. This work reports the continuation of our previous work on Cu@sub x@Cd@sub 1-x@Te@footnote 1@ and on Cd-Cu-Te-O systems@footnote 2@ by presenting the structural, optical and electrical properties of (CdTe)@sub x@Cu@sub y@O@sub z@ films grown by reactive rf-magnetron co-sputtering; it is shown that the optical and charge transport properties may be tailored by changing the relative concentration of the four elements. The films were obtained by co-deposition from CdTe and Cu targets under a controlled oxygen flow rate of 11 sccm. The power applied to the Cu target was 0, 10, 20, 30, 40, and 50 W, for different runs. The X-ray diffraction patterns indicated that the films are a mixture of CdTe-type cubic/hexagonal phases; however, it was observed that the hexagonal phase was favored for higher copper concentrations. The chemical composition was analyzed by energy dispersive spectroscopy. The results indicated that the atomic concentration of Cd and Te has nearly identical values in all samples, and decreases as the copper concentration increases from zero to 25 at.%. For films grown with 40 and 50 W in the copper target x=y=z=0.25. The bandgap varied from 1.62 eV (no Cu) to 1.48 eV (25 at.% Cu), a value quite appropriate for the absorbing layer in a solar cell. The four probe method was useful to determine the p-type resistivity of the films grown with Cu powers of 20 W and above. The values obtained ranged from 1.6 x10@super 3@ to 6.5x10@super -3@ ohm-cm. @FootnoteText@ @footnote 1@ S. Jiménez-Sandoval, S. López-López, B.S. Chao, M. Meléndez-Lira, Thin Solid Films 342 (1999)1.@footnote 2@ S. Jiménez-Sandoval et al., To be published (2005).

TF-MoP39 Influence of Ga Doping Level on the Properties of ZnO-Gax Films prepared by Radio Frequency Magnetron Sputtering*, H.C. Pan, C.Y. Su, C.N. Hsiao,* National Applied Research Laboratories, Taiwan*; S.-P. Lin,* ***C.-S. Chiou,*** Yuan Ze University, Taiwan

Gallium doped zine oxide (GZO) thin films are prepared by radio frequency sputtering on the Corning glass using a co-sputtering technique varying sputtering power of Ga@sub 2@O@sub 3@ target as the Ga doping source. The structural, electrical and optical properties of the GZO films are investigated in terms of the deposition conditions such as the Ga@sub 2@O@sub 3@ content in the film, partial oxygen pressure (O@sub 2@ /Ar ratio), film thickness, working pressure and film thickness. The optical and the electrical properties of GZO films were investigated by spectrometer, Hall effect measurement, X-ray diffractometery (XRD), atomic force microscopy (AFM), conducting atomic force microscopy (CAFM) and X-ray absorption near-edge spectroscopy (XANES). The deposited GZO films at room temperature were polycrystalline with a hexagonal wurtzite structures and preferential orientation along (002) plane, regardless of the Ga content. The crystallinity and grain size of the IZO showed an increasing tendency as function of the film thickness. The resistivity of the GZO prepared with around 2 wt.% Ga content in film composition is about 8x10@super -4@ @ohm@-cm and depends on the Ga doping level. The average optical transmittance of a 30 nm-thick film in the visible region (400 nm ~ 700 nm) is about 85%. The optical band gap depends on the Ga doping level is in the range of 3.4 ~ 3.5 eV. Chemical change of different Ga doping level in zinc oxide films was investigated using XANES. Intensities of the peaks appearing at the same energy of ZnO in XANES spectra were decreased with the Ga doping level.

TF-MoP41 The Effect of Ion-beam Assisted Deposition on the Electrical Properties of Indium Zinc Oxide Thin Films Investigated by Conducting Atomic Force Microscopy*, C.Y. Su,* National Applied Research Laboratories, Taiwan*; H.C. Pan,* National Applied Research Laboratories*; M.H. Shiao, C.N. Hsiao, K.N. Lee,* National Applied Research Laboratories, Taiwan

Indium zinc oxide (IZO) thin films with 5 wt.% and 10 wt.% of zinc oxide were prepared as the anode layer for organic light emitting diodes (OLEDs). The film deposition process gave a significant influence on device characteristics, and considerable improvements due to the energetic ion bombardments during ion-beam assisted deposition (IAD) were obtained. These improvements are even over the conventional vacuum deposition results. The conducting atomic force microscope (CAFM) that was self-established from a commercial atomic force microscope at ITRC (Instrument Technology Research Center) was employed to investigate the surface morphologies and corresponding electrical properties. And the experiment results suggest that the IAD has the possibility of controlling two factors: the growth morphology and surface electrical properties of the IZO thin films. Including lower roughness (Rms changed from 2.15 nm to 1.50 nm) and higher conductivity (>10@super 3@ @ohm@@super -1@cm@super -1@). The IAD gave uniform surface coverage, which means the initial film growth topography consist of well-distributed small grains other than coagulated islands. The current images that were simultaneously scanned and captured with the topographic images indicate improvement of surface electrical properties from the nano-scale surface inspection of the IZO thin films. The basic principles and mechanisms of this CAFM system are also described.

TF-MoP42 Optical and Electrical Properties of Sc-doped ZnO Thin Films Prepared by RF Magnetron Sputtering*, M.H. Shiao,* National Applied Research Laboratories, Taiwan*; C.C. Jaing, Y.J. Huang,* Ming Hsin University of Science & Technology, Taiwan*; H.C. Pan, C.Y. Su, C.N. Hsiao, K.N. Lee,* National Applied Research Laboratories, Taiwan

Scandium-doped zinc (ZnO:Sc) oxide thin films were prepared on Corning 1737 glass by r.f. co-sputtering of ZnO and Sc@sub 2@O@sub 3@ targets at various deposition temperatures ranging from room temperature (RT) to 300°C and different oxygen partial pressures. Composition of the ZnO:Sc thin films was analyzed by energy dispersive X-ray spectroscopy (EDS), and the crystalline structure was examined by X-ray diffraction (XRD). Optical transmittance of the films was measured by a Perkin Elmer Lambda 900 spectrometer. Electrical resistivity, Hall mobility and carrier concentration were investigated by a Hall effect measuring system. Surface morphologies and corresponding electrical properties of ZnO:Sc thin films were observed by adopting a conducting atomic force microscope (CAFM). From experimental results, the deposited thin films showed good conductivity (@>=@ 10@super 2@ @ohm@@super -1@cm@super -1@) and high optical transmittance (@>=@ 85%) in the wavelength range of 400-800 nm. The resistivity of ZnO:Sc thin films increased and the preferred orientation was changed from (002) to (103) as the oxygen partial pressure increased.

TF-MoP43 Characteristics of High-k Gate Dielectric Formed by Oxidation of Multi-layered Metal Films Deposited Directly on the Si Substrate by Sputtering*, M.T. You, S.-W. Jeong, H.J. Lee,* Sungkyunkwan University, Korea*; Y.-H. Roh,* Sungkyunkwan University, Korea, Republic of Korea

Recently, we demonstrated that the oxidation of the Hf metal film deposited directly on the Si substrate by sputtering results in the HfSi@sub x@O@sub y@/HfO@sub 2@ stack layer with excellent electrical properties and high thermal stability in direct contact with Si. In this work, we further investigated the physical and electrical properties of high-k oxide films obtained by the oxidation and annealing of the multi-layered metal films (e.g., Hf/Zr/Hf, Zr/Hf/Zr, etc.) Thin metal films with the typical thickness of 1-2nm were deposited on the Si substrate alternately by rf-magnetron sputtering. Oxidation was performed at 500°C for 120min using the conventional furnace under O@sub 2@ ambient. Post oxidation annealing was done at several temperatures (i.e., 500, 700, and 900°C) for 90sec using a rapid thermal processor(RTP) under either N@sub 2@ or O@sub 2@ ambient. Data of HF C-V, I-V and Fowler-Nordheim tunneling (FNT) electron injection were analysed. TEM and XPS techniques were used to investigate the structural changes of the high-k films due to post oxidation annealing. The multi-layered high-k oxide films were formed after oxidizing the multi-layered metal films deposited directly on the Si substrate. The subsequent RTP annealing at high temperature (700°C) not only results in the poly-crystallization of the multi-layered high-k oxide films, but also causes the inter-diffusion of either Hf or Zr, resulting in the multi-layered high-k gate oxide. For example, HfSi@sub x@O@sub y@/HfO@sub 2@/intermixed-layer(IL)/ZrO@sub 2@/intermixed-layer(IL)/HfO@sub 2@, films were formed, if the Hf/Zr/Hf metal films were oxidized and subsequently annealed. The inter-diffusion of metal atoms improves electrical properties in general. In addition, the data obtained from the FNT electron injection either from the gate electrode or from the Si substrate indicate that the defect density changes depending on the annealing conditions.

TF-MoP44 Characterization of Barium Zirconium Titanate Thin Films as Tunable Materials Prepared by rf Magnetron Sputtering*, W.-A. Lan,* National Tsing Hua University, Taiwan, R.O.C.*; T.-B. Wu,* National Tsing Hua University, Taiwan, R.O.C., Republic of China

There are a large number of perovskite structure ABO@sub 3@ ceramics with nonlinear dielectric properties being studied. For Ba(Zr@sub x@T@sub 1-x@)O@sub 3@ (BZT), with increasing the Zr content, the dielectric constant decreases and the leakage current is reduced by suppressing the formation of Ti@super 3+@ and hopping conduction. The Zr@super 4+@ ion is chemically more stable than the Ti@super 4+@ and has a larger ionic size to expand the perovskite lattice and shifts the ferroelectric-to-paraelectric phase transition temperature toward room temperature. In this work, the sputtered BZT ferroelectric thin films with different Zr substitution under several deposition conditions were investigated. The BZT thin films were deposited by rf sputtering using a 2 inch target. The test structure was made in M-I-M structure. The bottom electrode is (001)-textured LaNiO@sub 3@ (LNO) conductive oxide which was deposited on the Pt/Ti/SiO@sub 2@/Si substrate by rf sputtering with a thickness of 200nm. The Ba@sub x@(Zr@sub y@Ti@sub 1-y@)O@sub 3@ targets were prepared by solid state mixing method using single phase calcined powders x of BaZrO@sub 3@ and (1-x) Ba@sub 2@TiO@sub 4@. The mixing ratio , x, were 0.15, 0.2, 0.25. The sputtering was conducted under different rf-sputtering power, substrate temperature, Ar/O@sub 2@ ratio and target stoichiometry. The deposition time was controlled at 1 hour to study the effects of sputtering conditions. Platinum top electrode of 75 nm thick was deposited by rf sputtering at room temperature. Lift-off process was used to defined the pattern in circles with different radius. The crystalline phases of the films were examined with x-ray diffraction. Cross-sectional morphologies and thickness of the films were examined by field emission SEM. The dielectric properties of the films were measured with 4192A from 1 kHz to 1MHz. The voltage dependence of dielectric constant and loss tangent was measured with 4284A at 1 MHz.

TF-MoP45 Electrical and Optical Characteristics of MIS Structure using the a-C and a-C:H Films Grown by Closed-Field Unbalanced Magnetron Sputtering*, Y.S. Park, B. Hong,* Sungkyunkwan University, Korea

With extreme hardness of diamond and synthetic diamond-like carbon (DLC), carbon based materials were used mainly as a cutting tool coating and as an abrasive material. Since then, carbon based materials have been expanded into the market of electronics, optics and acoustics as well as coatings due to excellent electrical properties. Amorphous carbon (a-C) and hydrogenated amorphous carbon films were deposited on p-type silicon and glass substrates by a closed-field unbalanced magnetron (CFUBM) sputtering method. We have investigated the effect of various DC bias voltages on microstructure, electrical conductivity and optical properties. The samples were characterized with Raman spectroscopy, XPS, electrical resistivity, current-voltage (I-V) and capacitance-voltage (C-V) curves, UV-visible and FT-IR. The a-C and a-C:H films prepared by CFUBM sputter in this study show good conducting properties.

TF-MoP47 Thermochromic La@sub 1-x@Sr@sub x@MnO@sub 3@ (x = 0.1, 0.175, and 0.3) Smart Coatings Grown by Reactive Pulsed Laser Deposition*, M. Soltani, M. Chaker,* INRS-Energie, Matériaux et Télécommunications, Canada*; X.X. Jiang, D. Nikanpour,* Canadian Space Agency, Canada*; J. Margot,* Université de Montréal, Canada

Thermochromic Sr-doped LaMnO@sub 3@ thin films exhibit a metallic-to-insulator phase transition from low to high temperature. The transition temperature can be controlled by varying the concentration of Sr@super 2+@ ions dopant in the films. Using a reactive pulsed laser deposition (RPLD) process, we have successfully fabricated thermochromic La@sub 1-x@Sr@sub x@MnO@sub 3@ (LSMO) smart coating at relatively low deposition temperature (about of 500 °C), and without post-annealing. Silicon (100) and sapphire (1000) were used as substrates in order to study the substrate effect on the deposited films. The RPLD of LSMO films was performed in a background gas mixture of Ar and reactive O@sub 2@, from three La@sub 1-x@Sr@sub x@MnO@sub 3@ targets with different Sr doping concentrations (i.e. x = 0.1, 0.175, and 0.3). It was found that the deposited LSMO films perfectly adhere to the wurtzite Al@sub 2@O@sub 3@ as well as to the cubic Si substrate. Their perovskite structure was confirmed by X-ray diffraction (XRD). The composition of LSMO coatings was investigated by X-ray photoelectron spectroscopy (XPS) analysis of the La, Sr, Mn, and O bands. The metal-to-insulator phase transition of LSMO-coated sapphire was investigated by measuring the temperature dependence of the sheet electrical resistivity using the standard four-point probe technique. At room temperature, a thermal coefficient of resistance (TCR) about -1.5 % per °C was achieved in these films. Finally, the potential applications of these thermochromic smart coatings will be discussed.

TF-MoP48 TiN and TiO@sub2@:Nb Thin Film Preparation using Hollow Cathode Sputtering with Application to Solar Cells*, S.Y. Guo,* Energy Photovoltaics, Inc.*; W.N. Shafarman,* University of Delaware*; A.E. Delahoy,* Energy Photovoltaics, Inc.

Hollow cathode sputtering has found many applications for deposition of functional thin films. In particular, excellent TCOs, including In@sub 2@O@sub 3@:Ti, have been produced by reactive-environment hollow cathode sputtering.@footnote 1@ Recently, we have investigated titanium-based thin films using similar methods. TiN is well known for its excellent conductivity, inertness, and good optical reflectivity at long wavelengths. These properties make it a potential IR-reflective back contact material suitable for ultra-thin CIGS solar cells. Using a pulsed power, linear hollow cathode source, TiN films on Mo-coated glass were achieved by adopting a combination of four critical parameters. Two of these were the passing of nitrogen through the cathode cavity and magnetic field assistance. Electrical and optical properties of the films were measured. The optical emission spectrum of the Ar/N@sub 2@/Ti plasma and film XRD measurements will be reported. The effect of deposition parameters such as nitrogen flow rate, pressure, substrate bias and substrate temperature have also been studied. CIGS solar cells have been successfully fabricated on TiN and a conversion efficiency of 11.7% has so far been achieved. Transparent and somewhat conductive TiO@sub 2@ films doped with Nb were also prepared. The electrical and optical properties of these films will be reported. @FootnoteText@ @footnote 1@ A.E. Delahoy and S.Y. Guo, J. Vac. Sci. Technol. A, Jul/Aug 2005.

TF-MoP49 Optical Constants of (CdTe)@sub 1-x@Al@sub x@x Thin Films*, J. Jimenez Montecinos,* UAM-Azc., Mexico*; **A. Mendoza-Galvan,*** Cinvestav-IPN, Mexico*; M. Zapata-Torres,* CICATA-IPN, Mexico*; S. Jimenez-Sandoval, M. Melendez-Lira,* Cinvestav-IPN, Mexico

We have prepared (CdTe)@sub 1-x@Al@sub x@ thin films by R.F. co-sputering in order to evaluate their capability as a photovoltaic material. CdTe and Al were employed as targets. Samples were deposited on commercial glass substrates at substrate temperature of 400 °C. The aluminum content was controlled through the R.F. power intensity applied on the aluminum target. Samples were characterized by X-ray diffraction and EDX. Surface morphology, monitored by atomic force microscopy, showed a dependence with preparation details. A blue band gap shift is clearly observed by absorption spectroscopy as function of aluminum content of the films. Raman spectroscopy present a FHMW increase and small shift toward high wavenumbers in the LO CdTe-like mode. From ellipsometry measurements we obtained the pseudo dielectric function obtaining information about the critical points. Ellipsometry results also shown the shift in critical point energies as function of aluminum content. @FootnoteText@ @footnote 1@ Work partially funded by CONACyT-Mexico.

TF-MoP50 Inhomogeneous Rarefaction of the Process Gas in a Direct Current Magnetron Sputtering System*, **F.J. Jimenez**, S.D. Ekpe, S.K. Dew,* University of Alberta, Canada

The interactions between energetic particles and the sputter gas in a magnetron sputtering system have strong effects on the growth, structures and properties of the film. These interactions result in inhomogeneous rarefaction of the gas in the space between the target and substrate, and affect the transport of particles towards the substrate. A hybrid Monte Carlo and fluid model is developed to simulate 3-dimensional gas rarefaction due to the sputtering of metals in Argon, Neon and Krypton. The governing equations are solved iteratively in a 3D space with a non-uniform grid (octree). Collision events between the sputtered particles and the process gas are assumed as the dominant source of gas heating, however, the effect of the reflected neutrals is also included in the model. Gas rarefaction profiles have been predicted for different process conditions. Results compare well with experimental results. The location of the highest rarefaction depends strongly on pressure, power, target material and location of the substrate plane relative to that of the target. The extent of rarefaction depends further on the thermal conductivity of the gas. Materials with high sputtering yield, like Silver, show more rarefaction than those with low sputtering yield, like Tungsten and Aluminum. Tungsten, as a result of a higher target to gas mass ratio, shows more of the effect than Aluminum. For a 75 mm target at 300 W and 10 mTorr a rarefaction of about 65% is obtained for the sputtering of Aluminum in Argon gas, with the substrate plane located at 10 cm in front of the target.

TF-MoP51 Influence of Flux Anisotropy on Microstructure of Sputter Deposited Cr Films*, **S.Yu. Grachev**, J.-D. Kamminga, G.C.A.M. Janssen,* Netherlands Institute of Metals Research, the Netherlands

Sputter deposition is widely used to produce metal and compound thin films. The immanent feature of sputter deposition is that the arriving flux possesses a wide angular distribution. The flux distribution at the coated surface is influenced by the pressure of sputtering gas and by the tilt/rotation of the substrate. It is known, that the anisotropy of the flux distribution can become a source of anisotropic microstructure and, as a consequence, the anisotropy of film properties. In our study we concentrated on the influence of the flux anisotropy on the microstructure of Cr films. There are several sources for anisotropy in the Hauzer HC 750 industrial deposition system we used. First, the elongation of the target (600x120mm@super 2@) induces a flux distribution with arriving angles up to 60° to the substrate normal. This flux distribution results in strong anisotropy of the surface morphology and in-plane crystallographic texture. Second, we tilted the substrate around an axis parallel to the target elongation. This introduced anisotropy in the perpendicular direction. As a consequence, the in-plane texture of the film was turned by 90° with respect to the texture in films grown on substrates parallel to the target. Planetary rotation around axes parallel to the target elongation was also studied. The tilt of the columnar microstructure of samples on tilted substrates is dependent on Ar pressure. At low Ar pressure the tilt is close to the substrate tilt (43° for 45° substrate tilt). The tangent rule predicts the inclination of 26.5°. The discrepancy is attributed to the complicated flux angular distribution from the elongated target. At higher Ar pressure the tilt of the columnar structure was smaller due to the smearing out of the flux distribution.

TF-MoP52 Plasma Diagnostics of Inductively Coupled Plasma Assisted Magnetron Sputtering for Reactive Deposition of MgO*, **J. Joo**,* Kunsan National University, Korea

Real time process diagnostics for reactive deposition of MgO were done to optimize high deposition rate and high transparency of the deposited films in rectangular (5 inch x 25 inch) target system. Inductively coupled plasma was adopted to enhance reactivity of oxygen for low temperature deposition of MgO. Using bipolar pulse power supply at 150 kHz, depositiion rate of 30 nm/min was achieved with 500 W pulse and 300 W of ICP power, which gave 90% of UV/VIS transparency(300 nm - 800 nm). For more intelligent feedback control, several real time diagnostics including OES, discahrge voltage and current waveform, QMS were carried out. With aid of ICP, metal ion signal showed very strong correlation with the reactivity of the plasma.

Applied Surface Science
Room 206 - Session AS+BI-TuM

Surface Characterization of Organic and Biological Systems

Moderator: R.T. Haasch, University of Illinois

8:20am **AS+BI-TuM1 Synthesis and Characterization of Mixed Polymer Brush Films*, D.J. Dyer,*** *J. Feng,* Southern Illinois University*; R.T. Haasch,* University of Illinois-Urbana Champaign*; V.-N. Wong,* Southern Illinois University **INVITED**

Chameleons respond to their environment by changing color so that they take on the characteristics of their surroundings. Smart organic films may also respond to environmental perturbations and adapt to their environment. In particular, polymer brush films have shown remarkable switching properties, especially when the films are within the ultra-thin region from 1-100 nm. These so-called polymer brushes are composed of polymers that are tethered to an inorganic substrate and may stretch out away from that substrate. Polymer brushes that are composed of more than one component are referred to as mixed, or binary brushes. Typically, the two different polymers are randomly distributed on the surface and exhibit phase-separation and interfacial morphology that is distinct from that of spin-cast blends of the same composition. This occurs because the brush chains are confined to the substrate and are forced into contact with nearby incompatible chains, whereas in a blend the polymer chains can more easily rearrange during annealing. Here we discuss the synthesis and characterization of mixed polymer brushes on silicon and gold substrates. One of the major challenges we face is the quantification of the bulk film composition as compared to the air/liquid interface. For this we use a tandem XPS/RAIRS strategy. Our paper will place an emphasis on amphiphilic systems where one polymer is hydrophilic and the other is hydrophobic. These results demonstrate that a mixed brush of polystyrene (PS) and polyacrylamide (PAAM) may switch from hydrophobic to hydrophilic in one minute at room temperature. Such rapid switching is highly unusual for mixed brushes.

9:00am **AS+BI-TuM3 Characterization of a Chemically Passivated GaAs Based Sensor Device in Air and Electrolytes***, S.M. Luber,* Walter Schottky Institut, TU Muenchen, Germany*; D. Gassull,* TU Muenchen, Germany*; D. Schuh,* Universitaet Regensburg, Germany*; M. Tanaka,* TU Muenchen, Germany*;* ***M. Tornow****, G. Abstreiter,* Walter Schottky Institut, TU Muenchen, Germany

Functionalized field effect devices are promising candidates to act as smart substrates for sensor applications. For a use in biological systems a functional layer has to provide stability against electrochemical decomposition, and allow effective coupling of the surface potential to the conductive channel. We present a resistor device passivated with a 4'-substituted 4-mercaptobiphenyl (MBP) self-assembled monolayer (SAM) for sensing applications. Base material is a GaAs-AlGaAs heterostructure containing a quasi 2D electron gas 60nm beneath the surface. In the first part of our study we investigated the influence of the MBP-SAM on the electronic surface properties of n-doped GaAs samples employing the Kelvin probe technique. We changed the dipole moment of the MBP molecules using various substituents (-H, -OH, -CH@sub 3@) and found a linear effect on the electron affinity. In the second part we tested the stability of the resistor device based on the GaAs-AlGaAs heterostructure in aqueous solutions. Whereas a bare device degraded rapidly the coated samples showed a remarkable increase in stability. Furthermore we characterized samples coated with monolayers with CH@sub 3@ (MBP-CH@sub 3@) and OH (MBP-OH) substituents in buffered electrolyte solutions with varying pH. For the MBP-OH coated sample, a change in pH induced a change in the resistance of the device. Interestingly, the sample grafted with an MBP-CH@sub 3@ SAM also showed a clear response on pH which can be attributed to the adsorption of OH@super -@ ions on CH@sub 3@ groups.

9:20am **AS+BI-TuM4 Ion Beam Alignment of Nematic Liquid Crystal on PPV-layer*, S. Pylypenko,*** *K. Artyushkova, J.E. Fulghum,* The University of New Mexico*; O. Buluy, T. Prokopenko, Y. Reznikov,* Institute of Physics of National Academy of Sciences, Ukraine

The development of LCD technologies requires homogeneous alignment of liquid crystals (LCs). The traditional rubbing procedure, consisting of unidirectional brushing of the aligning substrates, is quite reliable but has some drawbacks, including the production of electrostatic charges and dust during the rubbing. Ion and plasma-beam alignment are among the more promising candidates to replace the rubbing procedure. Ion beam alignment is based on an angularly selective destruction and rearrangement of the surface material as a result of ion bombardment, creating orientational order on the initially isotropic surface. Here we report on effective alignment of LCs on an ion-bombarded PPV layer. Glass substrates covered with a thin layer of PPV were irradiated using 2KeV Ar@super +@ ions for varying times. The irradiated substrates were used to assemble planar cells, and the gap was filled with nematic LC 5CB. The measured value of the anchoring energy of ~ 3 10@super -3@ erg cm-2 appeared to be one to two orders of magnitude less than the typical value produced by plasma/ion-alignment. We found enhancement of the stability of the PPV layer in the irradiated area. The strong interaction of 5CB molecules with the PPV surface caused dissolution of the PPV by the LC, and the PPV-layer was not affected by LC in the irradiated region. Three-dimensional characterization of the polymer by X-ray Photoelectron spectroscopy (XPS), Angle Resolved XPS (ARXPS), and Confocal Microscopy (CM) utilizing multivariate analysis (MVA) techniques were carried out to study the mechanism of PPV alignment after ion-beam bombardment. Our results demonstrate that ion-beam treatment provides uniform alignment of liquid crystals characterized by a weak anchoring.

9:40am **AS+BI-TuM5 Plasma Beam Alignment for Liquid-Crystal Displays*, Y.-F. Chang,*** *C.-H. Lin, C.-W. Chen,* Industrial Technology Research Institute, Taiwan

Surface alignment of liquid crystals is an important issue in practical applications of liquid crystal (LC) cells on TFT-LCD process. The most common technique of LC alignment is an unidirectional rubbing on special polymer films which deposited on an conductive substrate such as ITO (Indium-Tin Oxide). The rubbing process has many disadvantages even though it has been widely used in the actual production of LCD. Thus, rub-free methods for LC alignment are strongly required in the next generation LCD technology. A number of non-contact LC alignment methods have been proposed in attempting to replace the rubbing process. And the well-known technique is ion beam irradiation proposed by IBM group. Another non-mechanical alignment technique, named photoalignment method, in which the UV light irradiation caused surface anisotropy of the bounding plates was studied for many years. The method was relatively simple, but the corresponding drawbacks such as weak anchoring energy as well as poor photo and thermal stability, may limit the application of this technology. In this research, a plasma beam alignment technique, in which the aligning substrate was treated with a flux of plasma that was extracted and accelerated electrostatically, was applied on the PI and diamond-like carbon (DLC) film. It is also a non-contact alignment process. The plasma flux was generated with a DC plasma source known as the anode layer thruster (ALT). The discharge channel was used to produce the sheet-like fluxes. The test panels (100 mm X 50mm) were fabricated with various plasma-beam processing parameters, w/o further passivation processes to study the alignment qualities including the pretilt angle, anchoring energy, VHR and Rdc as a function of these processing parameters. In addition, the measuring methods of these alignment qualities were also investigated in this study.

10:00am **AS+BI-TuM6 Measuring the Thickness of Organic/Polymer/Bio Films on Glass Substrates using Spectroscopic Ellipsometry*, H.G. Tompkins,*** *T. Tiwald, C. Bungay,* J. A. Woollam Co., Inc.*; A.E. Hooper,* Motorola, Inc.

In this work we discuss a method of determining film thickness for film/substrate combination where the index of refraction of the film and substrate in the transparent spectral regions are almost identical. Common examples of this situation are organic/polymer/biological films on glass substrates. IR ellipsometry is used and we use weight gain to provide some necessary additional information for determining the optical functions for the film material. The spectral regions of strong molecular vibrations are then used for determining film thickness.

10:20am **AS+BI-TuM7 Applications of Surface Analysis in the Medical Device Industry*, A.M. Belu,*** Medtronic, Inc.

The surface is an important zone as it is the interface between a material of interest and the environment with which it interacts. For biomaterials and drug delivery systems, knowledge of interface chemistry is important for understanding how a material will interact with the biological environment of the body. For other materials, particularly those that are employed in the manufacture of medical devices, evaluation of the surface is important to further understand issues with welding, adhesion, contamination, discoloration, etc. This talk will highlight the power of surface analysis methods and how they are employed in the medical device industry. The analytical methods include TOF-SIMS and ESCA which allow chemical characterization of the uppermost ~75Å of a material. Scanning probe microscopy (SPM) and laser profilometry are used to gain topographical information and to measure roughness of surfaces. A field emission scanning electron microscope (FE-SEM) allows high resolution imaging of surfaces with resolution capabilities to 1 nanometer. A low vacuum SEM further allows characterization of non-conductive, wet, and organic samples. SEM also has the capabilities for elemental identification and semi-quantitative analysis using an x-ray detector (EDS). Examples will be presented to demonstrate a range of surface analysis applications, from fundamental studies of biomaterials, to solving industrial problems. The power as well as the problems of data acquisition and interpretation will be highlighted with regards to each technique. Further, a comparison of all techniques will be made to help elucidate which method or methods are best for specific problems. Examples will include imaging the distribution of drug in a polymer coating (such as on stents), identifying contamination on medical devices (such as detergent residue on leads), evaluation of particles and defects, and characterization of surface chemical modification.

10:40am **AS+BI-TuM8 Microelectronic Multielectrode Interface for Evaluation of Living Cells***, **H.D. Wanzenboeck**, P. Hagl, K. Dominizi, E. Bertagnolli,* Vienna University of Technology, Austria*; E. Bogner, M. Wirth, F. Gabor,* University Vienna, Austria

*****PLEASE NOTE: YOU MUST IDENTIFY A DIFFERENT PRESENTER FOR THIS ABSTRACT. YOU MAY ONLY PRESENT ONE (1) PAPER AT THE CONFERENCE.*****Tests on living cells are crucial in biomedical research, biotechnology , pharmacological diagnostics and medicine, but applied methods are often labor-intensive. Microelectronic technology has available sensitive techniques for automatized, continuous measurement and data interpretation. These advantages are not made use of due to the complex nature of the interface between the biological and microelectronic world. This work describes the fabrication and fundamental application of a functionalized biomaterial interface. For an interface to biological substances the choice of suitable substrate materials is decisive. A biological layer of human ephitelial cells (Caco-2) was grown in-vitro on the interface. The biocompatibility of inorganic and organic materials typically used in microelectronics was exploited. Metals, dielectrics and semiconductors were evaluated qualitatively by optical imaging and by scanning electron microscopy at variable pressure. A quantitative evaluation was performed with biochemical tests on cell proliferation and differentiation. Fundamental aspects of bio-interface engineering are investigated by interface analysis methods. In a second step 3-dimensionally patterned surfaces were explored as interface to the biological world. By microstructuring a miniaturisation of typical structures in the range of 20 µm down to 1 µm - smaller than the diameter of a living Caco2 cell - was performed. A functional microelectrode array proved to be an excellent bio-interface to living cells. The growth and behaviour of a Caco-2 cell layer on this array of multiple microelectrodes was studied by optical and electrical measurements. The electrical measurement through a single Caco-2 cell was recorded as impedance spectrum. The results contribute to the further understanding of the interactions between living cells and microelectronic biosensors. This work provides fundamentals to unite microelectronic engineering with in-vitro biological studies.

11:00am **AS+BI-TuM9 Chemical Imaging of Biological Cells and Tissues using TOF-SIMS***, **P. Sjovall**,* SP Swedish National Testing and Research Institute, Sweden **INVITED**

Although time-of-flight secondary ion mass spectrometry (TOF-SIMS) has been used for chemical imaging of cells and tissues for almost 10 years, recent advances (notably the new primary cluster ion sources) have the potential to lead to a new breakthrough in this area. To realize this, however, additional research is required, addressing issues like (i) sample integrity, (ii) lateral resolution / detection efficiency, and (iii) sample complexity. We have used TOF-SIMS to record the spatial distribution of lipids in freeze-dried mouse brain sections and in surface-adhering polymorphonuclear leukocytes (PMNLs). The mouse brain sections (14 µm thick, cryosectioned, placed on a glass or Si substrate and freeze-dried inside the TOF-SIMS instrument or in a separate vacuum chamber) were analyzed using Au@sub n@@super +@ and Bi@sub n@@super +@ primary ions. It is demonstrated that TOF-SIMS analysis can provide detailed images showing the distribution of a number of lipids on the tissue surface at lateral resolutions down to < 1 µm.@footnote 1@ It is also shown that migration of lipids may be a problem under certain sample preparation and analysis conditions. The PMNLs were analyzed using a chemical imprinting technique, in which the outermost molecular layers of the cells are transferred to a substrate surface by pressing the substrate against the cell sample. The advantage of this method is that the substrate surface can be selected and/or functionalized in a manner that optimizes the subsequent imaging TOF-SIMS analysis. For the PMNLs, chemical imprints were made on Ag substrates in order to improve the detection yield and specificity of the lipids using Ga@super +@ primary ions (taking advantage of the Ag cationization). The resulting images show a complementary localization of cholesterol (plasma membrane) and phosphocholine (nuclear membrane).@footnote 2@ @FootnoteText@ @footnote 1@ Anal. Chem. 2004, 76, 4271@footnote 2@ Anal. Chem. 2003, 75, 3429.

11:40am **AS+BI-TuM11 Studying the Effect of Spacer Thiol Chemistry, Orientation and Surface Coverage on the Hybridization Properties of Mixed DNA SAMs on Gold***, **C.-Y. Lee**,* University of Washington*; P. Gong,* Colorado State University*; H.E. Canavan, L.J. Gamble,* University of Washington*; D.W. Grainger,* Colorado State University*; D.G. Castner,* University of Washington

Although it is desirable to capture DNA targets without purification from complex milieu (e.g., serum, tissue lysate) for microarray applications, this goal is often hindered by non-specific attachment of DNA and proteins. Minimizing nonspecific adsorption to biosensors and microarrays requires a non-fouling background. Furthermore, the coverage and orientation of DNA probes should be optimized for the capture of low concentrations of DNA via hybridization. To achieve each of these goals, we evaluated the effect that two spacer thiols [11-mercapto-1-undecanol (MCU) and 11-mercapto-undecyl tetra ethylene glycol (OEG)] have on surfaces prepared using singled-stranded DNA containing a thiol anchor group (SH-ssDNA). These mixed DNA self-assembled monolayers (SAMs) have been studied with X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure spectroscopy (NEXAFS), @super 32@P-radiolabeling, and surface plasmon resonance (SPR). Although XPS and radiolabeling indicate that SH-ssDNA surface coverage steadily decreases with longer exposure to the backfill molecules, NEXAFS indicates that polarization dependence peaks at short MCU and OEG exposure times (< 1h), after which polarization dependence decreases due to the loss of DNA from the surface. A comparison of hybridization responses from these probe surfaces was made using SPR by exposing the surfaces to complementary DNA in various concentrations of serum. SPR results indicate that although surfaces with MCU and OEG thiol spacers showed resistance towards non-specific DNA binding in pure buffer, hybridization efficiency is hindered by non-specific serum protein adsorption even at minimal serum concentration of 1%. Finally, differences in the hybridization property and protein resistance of the SH-ssDNA/MCU and SH-ssDNA/OEG mixed monolayer surfaces will be discussed.

DNA Topical Conference
Room 311 - Session DN+BI-TuM

DNA Surface Characterization

Moderator: D.W. Grainger, Colorado State University

8:20am **DN+BI-TuM1 First-principles Calculations of DNA Core Level Energies***, **J.M. Sullivan**,* Northwestern University and Naval Research Laboratory*; D.Y. Petrovykh,* University of Maryland and Naval Research Laboratory*; G.C. Schatz,* Northwestern University*; L.J. Whitman,* Naval Research Laboratory

X-ray photoelectron spectroscopy (XPS) is emerging as a powerful method for characterizing DNA on surfaces.@footnote 1@ The relative positions of core electron binding energies (CBEs) suggest likely binding geometries and strength of chemical bonds, and the peak areas provide a quantitative measure of the coverage. Although CBEs for simple molecules can often be readily assigned to specific adsorption sites and bonding configurations based on historical data, such interpretation for CBEs of DNA is not possible. As a start to developing a comprehensive ab initio understanding of DNA-surface interactions, we are using density functional theory to determine the geometric and electronic configuration of DNA nucleobases, nucleosides, and nucleotides in the generalized gradient approximation. We have initially focused on the nitrogen spectra because these are the easiest to interpret experimentally, arising solely from the nucleobases. Binding energies of core-electrons are evaluated in a variety of standard methodologies including spin-restricted and spin-unrestricted versions of Slater's and generalized transition state methodologies, and a @Delta@KS-type approach in which the CBE is determined directly by the difference between the total energy of the molecule with and without the core hole. We find the theoretical XPS spectra for isolated nucleic components are surprisingly similar to experimental spectra measured on DNA films, suggesting that-although the films are adsorbed on the surface-the underlying electronic structure of the nucleobases is "free-like". @FootnoteText@ @footnote 1@D. Y. Petrovykh, et al., J. Am. Chem. Soc. 125, 5219 (2003); D. Y. Petrovykh, et al., Langmuir 20, 429 (2004).

8:40am **DN+BI-TuM2 Entropic Recoil of Single DNA Molecules from Nanochannels*, J.T. Mannion*,** *C.H. Reccius, J.D. Cross, H.G. Craighead,* Cornell University

Entropic recoil of DNA molecules from pillar arrays has previously been reported.@footnote 1@ It has been shown that this effect has the potential to separate molecules according to length.@footnote 2@ A molecule straddling the interface between two microfabricated regions with vastly different volumes of configuration space experiences a force causing it to retract from the region which has less accessible volume. We have tested a device in which DNA molecules recoil from an array of channels as opposed to pillars. Nanochannels (100nm by 100nm) connected to the end of a microchannel (40 microns by 100nm) have been fabricated in a fused silica wafer. This change in geometry eliminates the possibility of herniation, which had previously been observed for molecules recoiling from pillar arrays. Using channels instead of pillars also makes it possible to track a molecule undergoing the recoil process more precisely and to carefully observe the dynamics of this process. As a consequence, we have been able to study the recoil and drag forces in greater detail. In addition we have clearly identified molecules that enter channels in a folded manner, and can observe unfolding events during recoil. @FootnoteText@ @footnote 1@ Turner, S. W. P.; Cabodi, M.; Craighead, H. G. Phys. Rev. Lett. 2002, 88, 128103-1-128103-4.@footnote 2@ Cabodi, M.; Turner, S. W. P.; Craighead, H. G. Anal. Chem. 2002, 74, 5169-5174. .

9:00am **DN+BI-TuM3 Surface Analysis Characterization of DNA-Microarray Chemistry*, L.J. Gamble,*** University of Washington **INVITED**

DNA microarrays have received considerable attention in the fields of bio- and nanotechnology due to their importance in the development of biosensing and diagnostic devices. The construction of these surfaces often entails the attachment of presynthesized oligonucleotides onto a derivatized surface. The hybridization efficiency of DNA microarrays and biosensors is determined in part by variables such as the density and orientation of the single stranded DNA oligomers used to build the devices. Surface analysis techniques such as X-ray photoelectron spectroscopy (XPS), near edge X-ray adsorption fine structure, time-of-flight secondary ion mass spectrometry (ToF-SIMS), and surface plasmon resonance (SPR) can aid in producing reliable, quantitative, and reproducible microarray chemistry. Our initial studies have used model surfaces of self assembled monolayers of thiolated DNA on gold to compare surface characterization (XPS and NEXAFS) of the DNA with hybridization efficiency (SPR and radio-labeling). Factors such as the DNA purity, DNA-surface interaction, and the non-fouling capabilities of the background are discussed. Commercial surfaces and surfaces modeled to simulate the commercial substrates are analyzed with surface analysis techniques as well.

9:40am **DN+BI-TuM5 Surface Science of DNA: The Time Has Come*, D.Y. Petrovykh,*** University of Maryland and Naval Research Laboratory **INVITED**

The development of practical DNA-based applications in bio- and nanotechnology has uncovered a menagerie of complications, many related to interactions of molecules with surfaces. Fortunately, the tools and methods developed or adapted for analyzing DNA and other biointerfaces are now significantly advanced to make an impact in both basic and applied surface science of DNA. I will focus on the progress in understanding DNA-surface and DNA-DNA interactions resulting from our ex-situ spectroscopic studies by XPS, FTIR, and NEXAFS. Homo-oligonucleotides have emerged as a useful model system for the study of such interactions. A few examples from the surprisingly wide range of phenomena that we have uncovered include polyelectrolyte behavior of weakly-interacting oligo(dT) strands, buffer-induced cross-linking in oligo(dC) films, and singularly high affinity of oligo(dA) for gold. The most practical impact of our analysis of DNA-functionalized surfaces has been quantifying the effects of experimental conditions (concentration, temperature, buffer salt, etc.) on DNA immobilization and hybridization. Improved understanding of nucleobase-dependent interactions should also facilitate the rational design of immobilization chemistries and DNA probe sequences. Ultimately, the challenge is to apply surface science methods to more complex biomolecular systems and processes, such as label-free characterization of DNA hybridization. @FootnoteText@ This work was done in close collaboration with A. Opdahl, H. Kimura-Suda, V. Perez-Dieste, J. M. Sullivan, F. J. Himpsel, M. J. Tarlov, and L. J. Whitman.

10:20am **DN+BI-TuM7 Kinetics and Thermodynamics of DNA Binding at Surfaces and in Solution*, R.M. Georgiadis,*** Boston University **INVITED**

This talk will review recent results on DNA oligonucleotide binding at surfaces and in solution. Using surface plasmon resonance spectroscopy for unlabeled oligonucleotide probes and solution oligonucleotide target species, we examine how the kinetics and thermodynamics of apparent binding for DNA/DNA hybridization depends on strand secondary structure, mismatches, and probe attachment chemistry. We show how SPR imaging can be used for quantitative monitoring of the kinetics of drug/DNA binding for an intercalating drug (actinomycin-D) interacting with array surfaces presenting multiple DNA target sequences containing different drug binding sites. SPR imaging is also used for optimization of attachment chemistry and for development of convenient surface coatings that resist non-specific binding of the pentapeptide containing drug. The array results are compared with solution phase measurements and other non-array SPR measurements and discussed in the context of chemical reaction mechanisms.

11:00am **DN+BI-TuM9 Measurement of RNA Density of States, Ionization Energy, Work Function and Charge Injection Barriers to Inorganic Materials***, M.M. Beerbom,* ***J.P. Magulick****, B. Lagel, A.J. Cascio, R. Schlaf,* University of South Florida

In light of recent conductivity measurements on single DNA stands, which yielded a wide range of results from insulating to metallic, it is interesting to investigate the electronic structure of oligonucleotides. In our experiments we directly measured the highest occupied molecular orbital (HOMO) density of states, the ionization energy, the work function and the charge injection barriers to graphite and Au of RNA homopolymers. This was achieved using photoemission spectroscopy (PES) in combination with clean multi-step in-vacuum deposition of RNA thin films using a homebuilt electrospray deposition system. This system allows the deposition of macro-molecular materials with a level of control similar to Knudsen cells directly from solution allowing essentially contamination free fabrication of thin films suitable for PES measurements. Furthermore, multi-step depositions without breaking the vacuum are enabled by this technique. Our presentation will give an introduction to the measurement technique, and introduce the experimental set-up. Data from several experiments on RNA homopolymer interfaces to graphite and Au will be discussed, and conclusions with regard to conductivity measurements made.

11:20am **DN+BI-TuM10 Compression and Free Expansion of Single DNA Molecules in Nanochannels*, C.H. Reccius*,** *J.T. Mannion, J.D. Cross, H.G. Craighead,* Cornell University

A variety of micromanipulation techniques have been used in the past to study the mechanical properties of DNA.@footnote 1@ Characterization of these properties is important for an understanding of DNA packing into chromatin or bacteriophage heads and also for the verification of theoretical biopolymer models. Extensive experiments have been conducted on stretching DNA in order to study its elasticity.@footnote 2@ In contrast to stretching by an external force, we are investigating the compression and subsequent free expansion of DNA molecules in artificial nanoscale devices. In this work, single lambda DNA multimers were driven through fluidic channels with a diameter of 100 nm by an electric field. Since the radius of gyration of the biomolecules was bigger than the channel diameter, their equilibrium state was no longer a sphere but instead an elongated cylinder.@footnote 3@ Forcing the stretched DNA into a channel constriction led to a compression of the molecule into a tight conformation. When the electric field was turned off, the DNA molecule slowly expanded back to the energetically favorable stretched out conformation. This expansion can be interpreted with the help of a simple polymer model based on self-avoidance effects. @FootnoteText@ @footnote 1@ Strick T. R., Dessinges M-N., Charvin G., Dekker N. H., Allemand J-F., Bensimon D., and Croquette V., Rep. Prog. Phys., 66, 1-45 (2003).@footnote 2@ Smith S. B., Finzi L., and Bustamente C., Science, 258, 1122-1126 (1992).@footnote 3@ Tegenfeldt J. O., Prinz C., Cao H., Chou S., Reisner W. W., Riehn R., Wang Y. M., Cox E. C., Sturm J. C., Silberzan P., and Austin R. H., PNAS, 101, 10979-10983 (2004).

11:40am **DN+BI-TuM11 In-situ Infrared Spectroscopic Study of Protonation of DNA Aggregated at Electrode Surfaces in Aqueous Solution*, K. Miyamoto*,** *K. Ishibashi, R. Yamaguchi, Y. Kimura, H. Ishii, M. Niwano,* Tohoku University, Japan

Recently we have proposed a method of monitoring hybridization of nucleic acids using infrared absorption spectroscopy (IRAS) in the multiple internal reflection geometry (MIR). The advantages of our method are follows: (1) Fluorescence labeling is not necessary for detection of DNA hybridization (label-free), (2) IRAS provide us with valuable information about conformations of biomolecules, and (3) MIR-IRAS enable us to in-situ monitor biomolecules in aqueous solution. We confirmed that hybridization of DNA can be detected through infrared spectral profiles: Formation of hydrogen bonding between complementary single-stranded (ss-) DNAs induced specific spectral changes in the frequency region of 1600-1750 cm@super -1@.@footnote 1@ Additionally, we demonstrated that when a positive potential is applied to the Si MIR-prism, negatively-charged ss-DNA molecules are aggregated on the prism surface, and that those aggregated ss-DNA molecules show infrared spectral profiles that are quite different from those of isolated DNA molecules floating in the solution. In this study, we have investigated the infrared spectral changes caused by DNA aggregation at an electrode (anode) surface in aqueous solution. By comparing previous IRAS data obtained for the base protonation under acidic condition, we determine that the observe spectral changes are due to protonation of the bases of DNA in the vicinity of the anode (Si MIR-prism) surface where electrochemical reactions generate a large number of protons. Results of ab-initio calculations support our interpretation. @FootnoteText@ @footnote 1@K. Miyamoto, K. Ishibashi, K. Hiroi, Y. Kimura, H. Ishii, M. Niwano, Appl. Phys. Lett. 86, 053902 (2005).

Electronic Materials and Processing
Room 310 - Session EM1-TuM
Defects, Interfaces, and Surface Passivation in Electronic Materials

Moderator: L.J. Brillson, The Ohio State University

8:20am **EM1-TuM1 The Role of Defects at Nanoscale Semiconductor Interfaces***, **Y.M. Strzhemechny**, H.L. Mosbacker, M.J. Hetzer, M. Gao, B.D. White,* The Ohio State University*; D.C. Look, D.C. Reynolds, C.W. Litton,* Wright-Patterson AFB*; M.A. Contreras, A. Zunger,* National Renewable Energy Laboratory*; L.J. Brillson,* The Ohio State University **INVITED**

Current understanding and control of semiconductor contacts increasingly require measurements sensitive to defects and chemical changes at nanoscale interfaces. We offer examples illustrating dramatic macroscopic effects occurring in semiconductor systems as a result of nanoscale interface phenomena. In some cases, there is an interplay of several competing defect-driven mechanisms. Elucidating them and finding the leading ones requires careful experimental approach. For single-crystalline ZnO, we study the role of near-surface defects on the formation of Au Schottky contacts. Among factors degrading rectifying characteristics of such contacts one should consider the following. High concentrations of shallow donors in the surface and subsurface regions lead to barrier thinning, resulting in increased tunneling. Alternatively, the presence of deep defects near contact interface promotes tunneling by defect-assisted hopping. Nanoscale electronic and chemical studies show that independent reduction of both shallow donors and deep defects significantly improves rectifying performance of the Au/ZnO contacts. We find that processing of ZnO with remote O and H plasma allows for controllable tailoring of chemical and physical properties of the surface. By the same token, nanoscale compositional and electrostatic variations between grain boundaries and grain interiors in thin polycrystalline films of Cu(In,Ga)Se@sub 2@, absorber layers in record-setting solar cells, show how nanoscale arrangement of near-surface stoichiometric defects may improve the overall photovoltaic efficiency. Confirming theory, we find a 50% reduction in Cu composition from grain interior to boundary and a p-type potential barrier that acts to reduce majority carrier hole recombination. These and related examples emphasize the practical significance of nanoscale chemical and electronic features at electronic material interfaces.

9:00am **EM1-TuM3 Interstitial Oxygen Related Defects and Current Leakage in UMOSFET on Epi/As++ Structure***, **Q. Wang**, M. Daggubati, H. Paravi,* Fairchild Semiconductor*; R. Yu, X. Zhang,* Lawrence Berkeley National Laboratory

Interstitial oxygen (O@sub i@) related defects and current leakage in UMOSFET on Epi/As++ structure has been investigated. The devices fabricated on heavily arsenic doped wafer with poly-silicon backside exhibited an increased yield loss in reverse current leakage with increasing O@sub i@ concentration in the wafer. For the wafers with the same O@sub i@ content, the leakage yield loss increases with decreasing device geometry. This leakage yield loss was attributed to the O@sub i@ related defects in active region (well junction). Transmission electron microscopy (TEM) study revealed, in the well junction region, the existence of extrinsic stacking faults and half-hexagonal dislocation punch-through defects, characteristic of oxygen precipitation. Defects created by the heavy body boron implantation seem to enhance O@sub i@ precipitation in the active region. In addition, the O@sub i@ is also found to diffuse to the interface of the poly-silicon layer and bulk silicon and precipitate out. This precipitation may consume the poly layer and reduce the gettering effect of poly silicon, which also leads to an O@sub i@ dependent current leakage. Similar experiments carried out with damaged backside wafers showed that current leakage yield loss was independent of O@sub i@ in the wafer and was low in general. The detailed TEM work indicated that the O@sub i@ did precipitate out in the bulk close to the back surface. The O@sub i@ precipitates may result in an intrinsic gettering and thus improve the current leakage yield. This comparative study between poly-silicon and damaged back-surfaces indicates that for heavily arsenic doped silicon wafers, intrinsic gettering is much better than extrinsic gettering due to the facts discussed above.

9:20am **EM1-TuM4 Control of Defect Concentrations in Silicon through Surface Chemistry***, **R. Vaidyanathan**, K. Dev, R.D. Braatz, E.G. Seebauer,* University of Illinois at Urbana-Champaign

Point defects govern many aspects of the behavior of crystalline solids, especially for semiconductors. We show through self-diffusion measurements that defect concentrations deep in the semiconductor bulk can be varied controllably over several orders of magnitude through submonolayer-level adsorption at the surface. For example, less than 0.01 monolayer of nitrogen adsorbed on silicon (100) that is undersaturated in defects lowers their concentration and inhibits diffusion, with the effects extending at least 0.5 µm into the bulk. The measurements have been made using a new method for determining key diffusion parameters via the short-time decay of an initial step concentration profile in an isotopic heterostructure. This method takes advantage of the relative ease with which step concentration profiles can be fabricated by thin film deposition, and in the limit of very short times provides particularly simple analytical means for obtaining parameters connected to diffusion length and defect formation. The adsorption phenomena discovered here open the possibility of precise defect engineering for numerous applications.

9:40am **EM1-TuM5 The Role of Etching in Film Growth during Wet Chemical Oxidation of H:Si(100)***, **K.T. Queeney**, J.W. Clemens, S.K. Green, C.A. Shea,* Smith College

Exposure of hydrogen-terminated Si(100) to aqueous solutions is an integral part of most wafer cleaning processes in microelectronics manufacturing. The quality of the thin oxide films formed (either intentionally or unintentionally) during this processing can have a profound effect on ultimate device performance. We have used transmission infrared spectroscopy to study this wet chemical oxidation of H:Si(100), allowing us to monitor both the evolution of SiH@sub x@ species and the growth of Si-O modes from the oxide film. While dissolved O@sub 2(aq)@ is the primary oxidizing species in H@sub 2@O, etching of the Si(100) surface by OH@super -@ species in the water plays an important role in oxidation. Sharpening of the Si-H bending modes in the earliest stages of oxidation suggests that this etching creates a more homogeneous surface, which is consistent with the high quality of the single layer SiO@sub x@ as judged by the evolution of Si-O optical phonons during oxidation. Studying the subsequent oxidation of surfaces first etched in deoxygenated water provides some temporal separation of the concomitant etching and oxidation processes and reveals that the relative reactivity of sites exposed by this etching is distinct from reactivity of analogous sites on extended Si surfaces, highlighting the importance of defect-driven chemistry during oxidation.

10:00am **EM1-TuM6 Experimental and Theoretical Studies of Various Oxides on the Ge(100)-2x1/4x2 Surface: Deposition of SiO and Oxidation by O@sub 2@ and NO***, **T.J. Grassman**, A.C. Kummel,* University of California, San Diego

To further the development of a germanium-based metal-oxide-semiconductor field effect transistor (MOSFET) a suitable gate-oxide material must be found which yields a high-quality, electrically-unpinned interface. For this, the semiconductor/oxide interface needs to be free of charge traps and other such interfacial defects that can cause Fermi-level pinning. Unfortunately, germanium's native oxide has been shown to be inadequate for the task of providing a clean, unpinned interface. We have investigated the bonding and electronic structures of various oxides on the Ge(100)-2x1/4x2 surface using scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and density function theory (DFT) modeling, including correction for the infamous DFT band gap problem. We will present atomically resolved images of the clean Ge(100) surface, the Ge(100) surface after oxidation with both O@sub 2@ and NO, the Ge(100) surface after deposition of SiO at various coverages, and the Ge(100) surface after nitridation with a neutral nitrogen plasma. Our STM and DFT studies show that SiO, unlike O@sub 2@ or NO, spontaneously forms an oxide bilayer by way of molecular SiO trimers, without displacing Ge atoms or oxidizing the surface. STS and DFT studies show this bilayer SiO absorption leaves the Fermi level unpinned. Such a bilayer formation makes SiO a strong candidate for use as a passivating buffer layer for further gate oxide growth. Conversely, NO and O@sub 2@ dosing causes Ge displacement and does not spontaneously form oxide or nitride bilayers.

10:20am **EM1-TuM7 Optimized Chemical Cleaning Method for Producing Device Quality Ge(100) Surfaces*, S. Sun,*** Stanford University*; Y. Sun, Z. Liu, D. Lee, S. Peterson, P. Pianetta,* Stanford Synchrotron Radiation Laboratory

Ge(100) surfaces treated by aqueous HF solutions with three different concentration (1:2, 1:5, and 1:25) have been systematically studied by synchrotron radiation photoemission spectroscopy (SR-PES) at Stanford Synchrotron Radiation Laboratory (SSRL). After HF treatment, the sample surface is hydrophobic and hydrogen terminated. HF solutions with higher concentration leave the Ge surfaces with less oxide, but relatively larger roughness. Hydrogen coverage also depends on the HF concentration. HF:H@sub 2@O (1:5) is a good choice, since it leads to a Ge(100) surface with approximately 0.9 monolayer hydrogen and less than 0.1 monolayer carbon and oxygen. The residual carbon and oxide come from the aqueous solutions. Solutions with higher concentrations of HF do not improve the surface cleanness. Additionally, a 10% HCl solution was also used to clean the Ge(100) surface. A hydrophilic and Cl terminated surface is achieved after HCl treatment. Relatively more residual carbon and oxide are left on the surface, which is due to the hydrophilic nature of treated surface. More details of the work will be discussed in the oral presentation.

10:40am **EM1-TuM8 XPS Study of Se-passivated Si(100)*, F.S. Aguirre-Tostado,*** *R.M. Wallace,* University of Texas at Dallas*; J. Zhu, G. Larrieu, E. Maldonado, W.P. Kirk, M. Tao,* University of Texas at Arlington

The presence of strained and dangling bonds on the atomically clean Si(100) surface leads to a metastable surface structure not suitable for the growth of high-k oxides. In the present work, we have examined the passivation of the Si(100) surface with one monolayer of selenium upon thermal annealing. Ex-situ analysis by x-ray photoelectron spectroscopy reveals that while Se-oxide formation is below the limit of detection, SiO@sub 2@ formation is observed. Assuming a 2D Se layer growth, we speculate that the formation of SiO@sub 2@ takes place at the atomic steps on the surface and at defect sites in the Se layer. It is also possible that there exists a cooperative inter-diffusion of Se and topmost Si atoms, leading to SiO@sub 2@ formation on top of the Se layer. From in-situ thermal annealing studies up to 425 °C, we find that adventitious C concentrations are below detectible limits above 100 °C while Se-Si and SiO@sub 2@ species surface concentrations remain unchanged. From photoelectron attenuation measurements, the SiO@sub 2@ thickness is around 8 Å. The mechanism of formation of the Se layer and SiO@sub 2@ will be discussed. This work is supported in part by the Texas Advanced Technology Program and SEMATECH.

11:00am **EM1-TuM9 Surface Passivation of Semiconductors*, D.R.T. Zahn,*** Chemnitz University of Technology, Germany **INVITED**

Considering GaAs(100) very often chalcogen atoms, i.e. sulphur and selenium, are employed for passivating its surface. Passivation can be achieved by exposing the surface to a beam of chalcogen atoms under ultra-high vacuum conditions or employing an ex situ wet chemical treatment followed by annealing in vacuum. We have studied both types of preparation using photoemission as well as Raman spectroscopies. Both techniques are capable of determining the change of band bending resulting from the passivation process. It is quite accepted that the chalcogen passivation induces a considerable reduction in band bending for n-type substrate material. However, the band bending is increased when p-type GaAs is used indicating that the density of surface states is changed but not removed from the band gap of the semiconductor. Core level photoemission data reveal that there are two distinct chalcogen atom environments on the passivated surface and that very similar surfaces are prepared independent on the preparation technique. The core level spectra provide very a very important input for DFT-LDA structure calculations which indicate that the reconstruction is likely to be different from the previously suggested chalcogen dimer terminated one. Moreover, we probe the passivated surfaces by addition of sub-monolayer coverages of organic molecules. The sharpening of core level spectra upon absorption of the molecules is indicative of some inhomogeneities in surface band bending being healed. Finally we address the influence of the passivation on electrical transport in metal/semiconductor structures.

Electronic Materials and Processing
Room 312 - Session EM2-TuM

High-k Dielectric Characterization

Moderator: G. Wilk, ASM America

8:20am **EM2-TuM1 Characterization of High-@kappa@ Materials using High Resolution Ion Backscattering*, T. Gustafsson,*** *E. Garfunkel, L.V. Goncharova, R. Barnes, D. Starodub,* Rutgers University **INVITED**

Understanding the thermodynamics and kinetics of film growth during fabrication of high-@kappa@ gate stacks is vital to establish atomic level control of interfacial layers and to minimize defects. Annealing such films in different atmospheres may lead to diffusion and reactions with significant consequences on the electrical properties. Ion beam methods, in particular medium energy ion scattering (MEIS), are non-destructive, high resolution (sub-nm) tools for quantitative characterization of buried layers and interfaces. An attractive feature is the possibility to use isotope tracing, which allows a study not just of the structures of such ultrathin films, but also of the processes responsible for their formation. We will discuss some key materials issues relevant to films and interfaces in next-generation highly-scaled CMOS gate stack structures as investigated using ion beams. As one example, we will contrast the behavior of Hf and Ce oxides on Si during annealing in an oxide atmosphere. The Hf based system shows evidence for oxygen exchange, which could be suppressed by mixing the oxide with SiO@sub 2@. Little SiO@sub 2@ interfacial growth was observed. This reaction saturates with time and appears to be enhanced after film recrystallization. Annealing in nitrogen results in reduced oxygen incorporation and exchange. In contrast, Ce silicates exhibit rapid interface growth upon oxygen exposure. Materials changes occur in the ultrathin films and at the various interfaces during growth and processing at elevated temperature that strongly affect device properties. Changes in oxide and silicate interface composition and thickness, phase mixing and crystallization within the film, and film decomposition will be discussed also for high-@kappa@ films on Ge and GaAs. In general the native oxides on these materials are less stable than those of Si, leading to different high-@kappa@ layered structures and interface composition.

9:00am **EM2-TuM3 Fermi Level Pinning at Re/HfO@sub2@ Interface and Effective Work Function of Re in Re/HfO@sub2@/SiO@subx@/n-Si Stack*, Y. Liang,*** *J. Curless, C. Tracy, D. Gilmer, J. Schaeffer, D. Triyoso, P. Tobin,* Freescale Semiconductor Inc.

One of the challenges in metal/high-k/Si based CMOS devices is a need for a metal with work function aligned with the Si valence band edge (5.2 eV) for PMOS devices. While a number of metals have vacuum work functions equal or greater than 5.2 eV, their effective work functions in a MOS structure are often less than 5.2 eV due largely to Fermi level pinning in the metal/high-k/Si stack. We used x-ray and ultra-violet photoemission spectroscopy (XPS and UPS) in conjunction with capacitance-voltage (C-V) measurements to investigate Fermi level pinning in a Re/HfO@sub2@/SiO@subx@/n-Si stack. Evolution of the Re vacuum work function at different Re film thickness and the resulting band bending in HfO@sub2@ and Si were determined by in situ XPS and UPS techniques. Results showed that the Re vacuum work function reached a constant value of 5.5 eV when the film exceeded 30 Å thick. Photoemission results further showed that the Fermi level at the Re/HfO@sub2@ interface was partially pinned, resulting in an interface dipole of 0.5 eV and a 5.0 eV effective work function with respect with HfO@sub2@sub. C-V measurement of the Re/HfO@sub2@/SiO@subx@/n-Si stack resulted in a 4.8 eV work function of Re with respect to Si. The difference in work functions determined by photoemission and by C-V will be discussed in terms of the contribution of additional interface dipoles in the Re/HfO@sub2@/SiO@subx@/n-Si stack.

9:20am **EM2-TuM4 Oxygen Diffusion and Reduction of Interfacial Layer in high-k Metal Oxide Gate Stacks*, L.V. Goncharova,*** Rutgers University*; M. Dalponte,* Universidade Federal do Rio Grande do Sul, Brazil*; T. Gustafsson, E. Garfunkel,* Rutgers University

Deposition of high-k metal oxide films onto Si substrates is accompanied almost unavoidably by the formation of a thin interfacial SiO@sub 2@ layer as a result of oxidation of the Si surface. This layer grows during metal oxide deposition in an oxygen-rich atmosphere or as a result of post-growth annealing treatments. Recently it has been found that deposition of an oxygen-gettering overlayer such as Ti on top of the high-k metal oxide can result in reduction and even possibly elimination of the SiO@sub 2@ interfacial layer. In our the work reported here we use Medium Energy Ion Scattering (MEIS) to focus on understanding (i) the diffusion and thermal stability of oxygen in multilayer high-k gate stacks and (ii) the reduction of interfacial SiO@sub 2@. HfO@sub 2@ films of different thickness were grown on Si(001) substrates with and without nitride incorporation on the interface. To study oxygen transport some of the films were re-oxidized in isotopically labeled @super 18@ O@sub 2@. The interfacial layer and the HfO@sub 2@ layer remain constant during deposition of the Ti overlayer at 300K, with the exception of a small amount of interdiffusion at the Ti/HfO@sub 2@ interface. There is no significant change in interfacial SiO@sub 2@. An ultra-high vacuum anneal (600K, P=10@super -9@ Torr) of the stack results in an immediate change in the oxygen region of the spectrum, accompanied by a lowering and broadening of Ti peak. This is clear evidence that some oxygen is moving towards the outer surface of the film and oxidizes Ti. The oxygen growth in the Ti layer occurs at least partially in parallel with a reduction of interfacial SiO@sub 2@ as it is suggested by a decrease of the interfacial Si peak. This process changes with increasing HfO@sub 2@ crystallinity, opening more permeable diffusive pathways via crystallite grain boundaries. Additional studies of the effects of nitrogen incorporation in the interfacial region and film thickness will be presented.

9:40am **EM2-TuM5 Characterization of High- and Low-k Dielectrics Materials using Secondary Ion Mass Spectrometry***, J. Bennett,* ATDF **INVITED**

The semiconductor industry continues to move forward with the introduction of high-k and low-k materials for use as gate dielectrics and interlayer insulators, respectively. The successful integration of these materials into the manufacturing process requires an understanding of the chemical, physical, and electrical properties of the new materials. Secondary ion mass spectrometry (SIMS) can provide valuable chemical information about high- and low-k materials, either using static SIMS to investigate surface chemistry or dynamic SIMS for depth profiling. However, these advanced materials are often complex mixtures of elements and physical phases that can complicate the analysis. This presentation will describe some of the current progress in the use of SIMS depth profiling to characterize both high- and low-k materials, and the challenges that remain. Examples from our lab will be used to demonstrate the difficulties (e.g., charging, beam damage) encountered when profiling new generation, porous low-k materials. Examples of backside SIMS to assess barrier metal diffusion will be also be shown. For high-k materials, particularly thin HfO@sub 2@ and HfSiO films, examples from our lab will be used to show the presence of several SIMS artifacts including preferential sputtering and sputter rate and ion variations. Also, the issue of dopant penetration through the films will be discussed.

10:20am **EM2-TuM7 Combined Electrical and Morphological Characterization of Al@sub 2@O@sub 3@ Films by Non-Contact AFM***, **J.M. Sturm**, A.I. Zinine, H. Wormeester, R.G. Bankras, J. Holleman, J. Schmitz, B. Poelsema,* University of Twente, The Netherlands

High-K Al@sub 2@O@sub 3@ films deposited on Si(001) by Atomic Layer Deposition (ALD) were investigated with non-contact AFM in ultra-high vacuum. Oxide charges in the film appear in the AFM images through the attractive interaction between the charge and its image charge in the conducting tip. The image contrast of the charge was found to depend on the tip-sample bias voltage. A spherical tip model based on the oxide charge, its image in the tip and the image of the tip in the substrate allows a quantitative description of the influence of the bias voltage. Most charges in the oxide film were identified as negative with a homogeneous depth distribution. Lateral variations of the Contact Potential Difference (CPD) and differential capacitance were recorded during acquisition of the topographic image with the aid of bias modulation and lock-in detection of the electrostatic force gradient at the first and second harmonic. CPD fluctuations with a typical magnitude of 20 to 50 mV on a lateral scale of ~50 nm were found. The lateral resolution of the CPD is limited with respect to the topography. This is attributed to charge screening with a length scale set by the effective Debye length. Al@sub 2@O@sub 3@ deposition on hydrogen-terminated Si (Si-H) resulted in a strong negative correlation between the differential capacitance and the surface topography (i.e. a large height correlates to low capacitance). For deposition on thermal SiO@sub 2@, this correlation was significantly reduced, whereas almost no correlation was observed for a SiO@sub 2@ film. The high correlation for deposition on Si-H is attributed to thickness variations due to substrate-inhibited ALD growth.

10:40am **EM2-TuM8 The Effect of Surface Pre-treatment upon the Growth of Hafnium Dioxide Layers on Silicon***, P. Mack, R.G. White, **J. Wolstenholme,*** Thermo Electron, UK*; T. Conard,* IMEC, Belgium

Angle resolved XPS (ARXPS) has been shown to be a powerful tool for the determination of the thickness of ultra-thin films. In the case of high-k dielectric layers, the technique is capable of measuring the thickness of both the high-k layer and intermediate layers of silicon dioxide or metal silicate. The values for layer thickness are in close agreement with those generated by a variety of other techniques. As well as knowing the thickness of these layers, it is important to determine whether the layers are continuous or whether the coverage of the high-k layer is only partial. Using ARXPS, a method has been developed to determine whether the coverage of the high-k material is continuous and, if not, to calculate the fraction of the surface that is covered. The method has been applied to HfO@sub 2@ layers produced using atomic layer deposition (ALD) on silicon wafers whose surfaces had received three different types of surface treatment. The way in which the layers grow and the nature of the resulting layer were found to depend upon the pre-treatment method. For example, growth on a thermal silicon dioxide surface resulted in complete coverage of HfO@sub 2@ after fewer ALD cycles than layers grown on an HF last surface. The results from ARXPS will be compared with those obtained from ToF SIMS that have been shown earlier to be a valuable alternative to the LEIS analysis.

11:00am **EM2-TuM9 Atomic Layer Deposition and Characterization of Hafnium and Aluminum Oxides and Hafnium Aluminates on Silicon***, **R.R. Katamreddy**, A. Deshpande,* University of Illinois at Chicago*; R. Inman, A. Soulet, G. Jursich,* American Air Liquide*; C.G. Takoudis,* University of Illinois at Chicago

In future minimization of transistor devices, alternative high dielectric constant materials are needed to replace SiO@sub 2@ and its first-generation replacement material- silicon oxy-nitride. Among the diverse number of possible candidates, HfO@sub 2@ and Al@sub 2@O@sub 3@ films are currently among the most promising replacement materials. Each of these materials has different advantageous and disadvantageous properties for the gate dielectric application. So a more optimal film may be a compositional mixture or nanolaminated structure of these two materials. In this study, the two oxide films are investigated individually on silicon in order to further investigate more complex combinations of the two metal oxides. Ultra-thin hafnium oxide and aluminum oxide films are grown on precleaned silicon substrate having approximately 10 Å residual oxide thickness. The deposition takes place in an ALD reactor using tetrakis(diethylamino)hafnium and tris(diethylamino)aluminum@footnote 1@ precursors respectively. The oxidizing co-reactant is water. After deposition, some of the resulting high-k films are annealed at 600 - 1000°C. Both deposition film and its interfacial region of annealed and non-annealed sample substrates are characterized using Fourier Transformed infrared spectroscopy, X-ray Photoelectron Spectroscopy, Scanning Transmission Electron Microscopy (STEM) and Electron Energy-Loss Spectroscopy in STEM. Our studies indicate that the as-deposited HfO@sub 2@ film is amorphous and there is no indication of silicate formation at the interface; upon annealing of these films, electron microscopy measurements reveal a novel interesting sequence of interfacial transformations as the temperature increases. Similar measurements on Al@sub 2@O@sub 3@ films will be discussed. Preliminary results on nanolaminate deposition of Al@sub 2@O@sub 3@ and HfO@sub 2@ films will also be presented. @FootnoteText@ @footnote 1@ US Patent Application Number 20050003662 A1 filed in May, 2004.

11:20am **EM2-TuM10 Measurement of Thicknesses of HfO@sub 2@, HfSiO@sub 4@, ZrO@sub 2@, and ZrSiO@sub 4@ Films on Silicon by Angle-Resolved XPS***, W. Smekal, W.S.M. Werner,* Vienna University of Technology, Austria*; **C.J. Powell**,* National Institute of Standards and Technology

We report on the use of a new NIST database for the Simulation of Electron Spectra for Surface Analysis (SESSA) in measuring thicknesses of candidate high-@kappa@ gate-dielectric materials (HfO@sub 2@, HfSiO@sub 4@, ZrO@sub 2@, and ZrSiO@sub 4@) on silicon by angle-resolved XPS. Practical effective attenuation lengths (EALs) have been computed from SESSA as a function of film thickness and photoelectron emission angle (i.e., to simulate the effects of tilting the sample). EALs have been calculated in two ways. First, realistic (Mott) cross sections have been used to describe the elastic scattering of the signal electrons in the substrate and overlayer film; appropriate inelastic mean free paths have also been selected for each material. Second, the transport approximation (TA) has been utilized in which isotropic elastic-scattering is assumed; in addition, it is assumed that elastic- and inelastic scattering parameters for the film can also be used for the substrate. These EALs have been compared with similar values obtained from the NIST Electron Effective-Attenuation-Length Database (SRD 82) that utilizes an algorithm based on the TA (and where it is again assumed that substrate and overlayer have similar scattering properties). Excellent agreement is found between EALs from SRD 82 and those from SESSA with the TA. Generally good agreement was found between these EALs and those from SESSA with the Mott cross sections, but there were some differences for film thicknesses less than the inelastic mean free path of the photoelectrons in the high-@kappa@ material. The SESSA EALs with the Mott cross sections are considered more reliable than those from the TA because realistic cross sections are used for both elastic and inelastic scattering in the film and substrate materials. These EALs should thus provide more accurate measurements of film thickness, particularly in applications where the film and substrate have different electron-scattering properties.

Magnetic Interfaces and Nanostructures
Room 204 - Session MI+NS-TuM

Magnetic Nanostructures, Surfaces, and Interfaces

Moderator: R.A. Lukaszew, University of Toledo

8:20am **MI+NS-TuM1 Size Effect and Chemical Ordering in [FePt]@sub 100-x@Cr@sub x@ Nanoparticles***, C. Srivastava,* ***G.B. Thompson,*** *J.W. Harrell, D.E. Nikles,* University of Alabama

FePt nanoparticles have received considerable attention as candidate materials for achieving ultra-high areal storage densities. Recent experimental and modeling studies have suggested that FePt must achieve a critical size near 4 nm for the chemically ordered L1@sub 0@ phase to be stable. We report the use of Cr in controlling the size and ordering temperature in FePt nanoparticles. Two series of [FePt]@sub 100-x@Cr@sub x@ nanoparticles (x = 5, 10 and 16 at. %) were chemically synthesized by a high-temperature salt-decomposition process yielding as-prepared diameters of 2 nm and 4 nm. XRD and STEM-EDS confirmed that the Cr formed a solid solution within the A1 FePt phase. Upon annealing, the as-synthesized 4 nm [FePt]@sub 100-x@Cr@sub x@ particles ordered at 450°C while maintaining ~4 nm size. In contrast, the as-synthesized 2 nm [FePt]@sub 100-x@Cr@sub x@ particles ordered at 550°C. It was noted that the initial 2 nm particles had achieved an ~4 nm sintered particle size at 550°C. Thus, the initial particle size is critical before chemical ordering can commence. Once the critical size is achieved, Cr was able to reduce the ordering temperature. The initial 4 nm FePt nanoparticles ordered at ~500°C and experienced rapid particle sintering at the onset of its ordering temperature. In contrast, the Cr alloyed nanoparticles were shown to have reduced grain growth at elevated temperatures. Magnetrometry measurements of the nanoparticles indicated that the coercivity is reduced with Cr content.

8:40am **MI+NS-TuM2 Core Size Effects on Core-Shell Structured Fe/FeO@sub x@ Nanopaticles***,* ***A. Ceylan***[1]*, S. Shah,* University of Delaware*; K. Hasanain,* Quaid-e-Azam University, Pakistan

In this study, we examined the particle size dependence of magnetic properties of Fe/Fe-oxide core/shell structured nanoparticles. Inert gas condensation has been used to synthesize the nanoparticles. Structural and magnetic properties of the samples have been investigated by various techniques. It has been observed that the effect of AFM shell can be relatively enhanced by decreasing the core size such that much higher exchange bias than larger particles is obtained. Furthermore, as an indication of pinned spins, which are attributed as one of the reasons of higher exchange bias field, at the AFM-FM interface, a vertical shift at the hysteresis loops has also been observed in small nanoparticles. Room temperature magnetic measurements have revealed that small particles show superparamagnetic behavior. However, the system does not reach to saturation even at 4T which indicates high anisotropy. These observations reveal that superparamagnetic behavior is related to the small size rather than a lack of anisotropy.

9:00am **MI+NS-TuM3 Magnetic Field Effects in Ferromagnetic/Organic Hybrid Structures***,* ***J. Shi,*** University of Utah **INVITED**

Spin injection/detection and coherent spin transport are key ingredients in Spintronics, which were first demonstrated in the giant magnetoresistance or GMR effect in all-metal systems. In this talk, I will present our recent progress using organic semiconductors. In spin valves consisting of two ferromagnetic layers (La2/3Sr1/3MnO3 or LSMO and Co) and an organic semiconductor spacer (Alq3), we have successfully shown electrical spin injection/detection and coherent spin transport through the GMR effect. In addition, we have also found a high-field magnetoresistance effect in these structures. Our work shows that this high field effect originates from the magnetic field enhanced carrier injection due to the anomalous Fermi level shift in double exchange ferromagnets such as LSMO.

9:40am **MI+NS-TuM5 Magnetic Stripes at the Spin Reorientation Transition of a Magnetic Thin Film***,* ***Z. Qiu,*** University of California at Berkeley **INVITED**

One fundamental issue in magnetic nanostructure research has concerned the presence of magnetic long-range order in a two-dimensional (2D) magnetic system. It has long been established that an isotropic 2D Heisenberg system does not carry long-range order at nonzero temperature. The magnetic order observed in ultrathin films is usually attributed to the existence of magnetic anisotropy. In an ultrathin film with perpendicular magnetocrystalline anisotropy, the spin direction could exhibit the so-called spin reorientation transition (SRT) from perpendicular to the in-plane direction of the film. At the SRT point, the perpendicular magnetocrystalline anisotropy is balanced out by the dipolar shape anisotropy and the system approaches to an isotropic Heisenberg system. Thus an investigation of the magnetic phase near the SRT point is expected to reveal the magnetic origin of 2D magnetic systems. In this talk, I will present an overview and our most recent experimental result on this subject. Using photoemission electron microscopy (PEEM) to do element-specific measurement, we studied the SRT in magnetically coupled sandwiches. We show that a crossover from the anisotropy length to the dipolar length governs the formation of the magnetic stripe phase.

10:20am **MI+NS-TuM7 Inhomogeneous Magnetic States in Gd/Fe and SmCo/Fe Nanolayers***,* ***D. Haskel,*** Argonne National Laboratory **INVITED**

The reduced size and dimensionality of layered magnetic nanostructures enhances the role that surfaces and interfaces play in determining their magnetic structures. This can result in inhomogeneous magnetic states, wherein the local magnetization varies with distance away from surfaces or interfaces. Using hard x-ray magnetic circular dichroism and x-ray resonant magnetic scattering, we explore the nature of such inhomogeneous states in Gd/Fe metallic multilayers and SmCo/Fe spring magnets. In collaboration with Y. Choi, J. Lang, D. Lee, G. Srajer, C. Kmety, J. Pollmann, C. Nelson, R. Camley, J. Meersschaut, J.S. Jiang, S.D. Bader Work at Argonne is supported by the U.S. Department of Energy, Office of Science under contract No. W-31-109-ENG-38.

11:00am **MI+NS-TuM9 Magnetic Quantum Tunneling and Relaxation in Molecular Magnets***,* ***L.J. de Jongh,*** *A. Morello, F. Luis, M. Evangelisti, F. Mettes,* Leiden University, The Netherlands **INVITED**

For strongly anisotropic magnetic clusters, like Fe@sub 8@ and Mn@sub 12@-ac, quantum tunneling of the cluster spins below their blocking temperatures T@sub B@ of a few K has been observed by several groups, and is expected to be triggered by the dynamic hyperfine interaction of the cluster spins with their surrounding nuclear spins, as recently predicted by Prokof'ev and Stamp.@footnote 1@ In that model, however, the ensuing relaxation of the electron spins is towards the nuclear spin system, leaving open the question if and at what stage, by which mechanism and at what rates the nuclear and electronic spin systems relax to the lattice phonons. That such phonon relaxation channels are indeed operative even deep in the quantum regime, could be proven unambiguously by our measurements of the specific heat contributions of both nuclear and electronic spin systems at temperatures T<<T@sub B@.@footnote 2-4@ Nuclear Magnetic Resonance is the technique of choice for studying the nuclear spin-dynamics involved in these processes. In addition, since the nuclear spins have to relax to the lattice via the electron spin system, also the dynamics of the latter is probed. In the talk such data (taken down to 20 mK), will be presented@footnote 5@ and analysed in the light of earlier developed theories for dynamic nuclear polarization and nuclear relaxation by paramagnetic impurities in insulating compounds, leading to new insights in the quantum relaxation mechanisms in molecular nano-magnets. @FootnoteText@ @footnote 1@ N.V. Prokof'ev and P.C. Stamp, Phys. Rev. Lett. 80, 5794 (1998). @footnote 2@ F.L. Mettes et al. Phys.Rev.

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[1] **Falicov Student Award Finalist**

B64, 174411 (2001);Phys. Rev. Lett. 85, 4377 (2000). @footnote 3@ M. Evangelisti et al. Phys. Rev. Lett. 93, 117202 (2004). @footnote 4@ A. Morello et al. Phys. Rev. Lett. 90, 017206 (2003). @footnote 5@ A. Morello et al. Phys. Rev. Lett. 93, 197202 (2004).

MEMS and NEMS
Room 207 - Session MN-TuM
Micro and Nano Fabrication Techniques for MEMS & NEMS

Moderator: A.V. Sumant, University of Wisconsin

8:20am **MN-TuM1 Nanomanufacturing Using Nanotemplates for Directed Assembly of Nanoelements*, A. Busnaina,*** Northeastern University*; J. Mead,* University of Massachusetts Lowell*; G. Miller,* University of New Hampshire*; C. Barry,* University of Massachusetts Lowell **INVITED**

The electronics industry is looking for new nanoscale technologies that will be energy efficient with high performance, scalable with gain and operational reliability at room temperature that are preferably compatible with CMOS process and architecture. Proposed nanoelectronic devices using technologies beyond currently-deployed are many; mechanical or molecular switches, spin logic, phase logic, molecular devices, cross-bar devices, cross-net devices, etc. Manufacturing of these involves very diverse fabrication and assembly techniques that may involve top-down, bottom or both. There is a need to develop heterogeneous process integration such as combination of hierarchical directed assembly techniques with other processing techniques. High-throughput hierarchical directed assembly and nanoscale components and interconnect reliability will also be essential in going beyond silicon. Another important nanomanufacturing issue is nanoscale defect mitigation and removal and defect tolerant materials, structures and processes in addition to nanoscale metrology tools, such as in-line or in-situ monitoring and feedback. Fundamental understanding and novel technology in high rate, high volume integration and assembly of robust tools and processes are addressed. Nanotemplates and tools are used to accelerate the creation of highly anticipated commercial products and will enable the creation of an entirely new generation of applications. This requires understanding what is essential for a rapid multi-step, high volume/high rate processes, as well as for accelerated-life testing of nanoelements and defect-tolerance.

9:00am **MN-TuM3 Ion Trapping in Microfabricated Ion Trap Arrays*, D. Cruz,*** UCLA and Sandia National Laboratories*; M. Fico, A.J. Guymon, R.G. Cooks,* Purdue University*; J.P. Chang,* University of California, Los Angeles*; M.G. Blain,* Sandia National Laboratories

In this work we describe the microfabrication and testing of cylindrical ion trap arrays. The ion trap has become an essential tool in several areas of physical science, including mass spectrometry, atomic frequency standards, studies of fundamental quantum dynamics, and quantum information science. Many of these applications benefit from miniaturized ion traps at dimensions several orders of magnitude below the current centimeter and millimeter scale. Our design of the individual trap array element consists of two endcap electrodes, one ring electrode, and a detector/collector plate, fabricated in seven tungsten metal layers by molding tungsten around SiO@sub 2@ features (0.5 µm minimum dimension) using standard lithography and plasma etching techniques. Each layer of tungsten is then polished back in damascene fashion. The SiO@sub 2@ is removed using a standard MEMS release processes to realize a free-hung ion trap element. Common anchor points of adjacent elements allow for the entire array of traps to be operated in parallel. Four different sized traps were fabricated with inner radius of 1, 2, 5 and 10 µm and heights ranged from 3-24 µm. We focused our testing on the 5-µm sized ion trap array to trap toluene (C@sub 7@H@sub 8@), mass 92 amu. We discerned the electrical characteristics of the packaged ion trap arrays through vector network analyzer measurements. We ejected the ions by turning off the rf and noted a current signal. We were not able to fully determine that our signal was all due to trapped ions. However, we attained favorable trapping conditions such as a significant pseudopotential well and an ionization rate twice the ion loss rate determined by simulation. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

9:20am **MN-TuM4 Monolithic In-Plane Tunable Optical Filter*, J. McGee,*** *N. Siwak, R. Ghodssi,* University of Maryland, College Park

The development and commercialization of future communication systems and biological diagnostic equipment will benefit greatly from dense integration of optical and electrical components through the use of in-plane, guided optics. Tunable optical filters are a necessary component for wavelength multiplexing and spectroscopy. However, in-plane devices have been challenging to produce as the very advantages of guided optics, small size and dense integration, lead to loss mechanisms that degrade the filter well below the performance of out-of-plane devices. Indium phosphide is our chosen material as its direct bandgap provides the possibility of integrated emitters and lasers while operating in the standard telecommunications bands of 1500-1600 nanometers at low loss. We recently demonstrated a functional in-plane tunable filter in indium phosphide and we have now improved its performance by utilizing a ribbed waveguide structure. The use of ribbed waveguides offers the advantage of a large beam less susceptible to divergence while providing single mode operation. In our device, an electrostatically-actuated doubly-clamped beam deflects a ribbed Bragg reflector relative to a stationary ribbed waveguide attached to a second Bragg reflector, forming a variable-length Fabry-Perot cavity. A simulation model we developed predicts a Q-factor of 90 compared to a Q-factor of 44 measured in the original device. The detailed fabrication, characterization, and measurement results will be presented.

9:40am **MN-TuM5 Cooper-Pair Molasses - Cooling a Nanomechanical Resonator with the Quantum Noise of a Single Electron Transistor*, K.C. Schwab,*** National Security Agency **INVITED**

We are performing ultra-low temperature experiments with a radio-frequency, nanomechanical resonator coupled to a superconducting single electron transistor, a system which has demonstrated the closest approach to the uncertainty principle for continuous position detection, and the closest approach to the quantum ground state of a mechanical system.@footnote 1@ Recently, we have used the resonator to detect the asymmetric, quantum noise of the SET, which produces the back-action required by the uncertainty principle. In addition, have discovered an unexpected cooling mechanism, analogous to optical molasses, which is a result of resonant Josephson effects in the transistor: we have observed cooling of a 10 MHz, Q=230,000 mode from 500 mK to 100 mK. Using these techniques and devices, we are anticipating the observation of squeezed, superposition, and entangled states of a mechanical device. @FootnoteText@ @footnote 1@LaHaye, Buu, Camarota, Schwab, "Approaching the Quantum Limit of a Nanomechanical Resonator," Science 304, 74 (2004).

10:20am **MN-TuM7 Granular Adsorbent Loading and Wafer Bonding for Si Microcavity Preconcentrator*, H.K. Chan,*** University of Michigan*; M. Takei,* Fuji Electric Systems*; S.W. Pang,* University of Michigan

A new technique for loading 180 to 212 µm diameter granular adsorbents and Au-Si eutectic bonding at 400 °C has been developed for filling and hermetically sealing 450 µm deep Si cavity microheaters for thermal regeneration of graphitized carbon adsorbents. This development has enabled the first wafer-level integrated, microfabricated preconcentrator for trapping parts-per-billion concentrations of volatile organic compounds (VOCs). Previous Si microheaters for preconcentrators have included anodically bonded glass and Si and Al solder bonded Si-Si using rapid thermal annealing at 850 °C, all of which were assembled at the die level due to the difficulty in loading carbon granules using dry filling methods. The newly developed adsorbent-solvent method uses the principle of solvent surface tension to confine the granules into the cavities. This method is demonstrated across a 100 mm wafer for cavities accommodating 0.8 to 1.5 mg of carbon granules. The remaining solvent in the porous carbons has to be removed to avoid outgassing during the wafer-level hermetic sealing step using Au-Si eutectic bonding. Solvent removal under vacuum and elevated temperature have been investigated for the new adsorbent-loaded cavity microheaters. The resulting bonded wafers after loading of carbons and removal of the solvent have bonding strengths of >3 MPa under a tensile load for Au-Si eutectic bonding at 400 °C. The result of the new adsorbent-solvent loading, solvent removal, and Au-Si eutectic bonding is the first wafer-level integrated microscale carbon granule preconcentrator which traps VOCs at room temperature and heats to 300 °C to thermally regenerate the carbons and desorb the VOCs for analysis with a microscale gas chromatograph.

10:40am **MN-TuM8 Copper Electroplating to Fill Blind Vias for 3D Integration*, S. Spiesshoefer*,** *S. Polamreddy, R. Figueroa, J. Patel, T. Lam, L. Cai, S. Burkett, L. Schaper,* University of Arkansas

The continued demand for lower cost electronic products with decreased size, higher performance and increased functionality require improvements in the system level integration of logic, memory, and other functional integrated circuits. The formation of vertical interconnects in silicon may be one approach to provide this integration. This method involves stacking of individual die to form a highly interconnected 3D structure. One way to create an efficient 3D stack is to place electrically conductive vias through the body of the silicon to bring the connections from top to bottom. Copper is the metal used to fill the through silicon via (TSV) structure because of the high conductivity and the common use in multilevel wiring. A process will be described in this paper to electroplate copper into small diameter (5-10 µm) vias of aspect ratio > 3. The objective of this project is to develop an electroplating process to obtain a void-free copper filled blind via. Prior to plating, vias are formed by both reactive ion etch (RIE) and deep RIE processes. The resulting via profile varies depending on the etch process chosen. Vias are lined with insulation, barrier, and seed films. The insulation, SiO@sub2@, is deposited by plasma enhanced chemical vapor deposition (PECVD) while the barrier (TaN) and Cu seed layers are deposited by sputtering. A complete and conformal copper seed layer is essential for the electroplating process. A combination of three electroplating techniques is used in this study. They consist of optimized bath composition (additive control), fountain plating, and reverse pulse plating. The goal during electroplating is to achieve a bottom-up fill, also referred to as a super fill. The process will be described that results in void-free electroplating to fill an array of blind vias as well as the related processing issues.

11:00am **MN-TuM9 A Fully Integrated Micro Plasma Electron Source in Silicon***, **E. Wapelhorst**, J.P. Hauschild, J. Müller,* Hamburg University of Technology, Germany

This paper presents the concept and the fabrication of a novel, fully integrated electron and UV light source using a micro plasma. The electron source is primarily developed for use in a micro mass spectrometer. This novel system is fabricated using standard processes in silicon e.g. DRIE based on the working principle of a micro plasma ion source as shown in.@footnote 1@ Furthermore, the RF-efficiency is increased by direct RF coupling through vias. An application of this type of electron source for ionization purposes in a micro mass spectrometer has been presented in,@footnote 2@ which uses the concept of.@footnote 1@ The electron source consists of three units: The filament, the plasma chamber, and the electron accelerator. The pressure in the plasma chamber is set to 100 Pa. To ignite a stable RF plasma in the chamber, a current pulse is driven through the filament to free electrons while the RF signal is directly applied to the RF coupler. After ignition the filament is switched off. By applying a voltage between the extraction grid and the acceleration grid electrons can be extracted from the plasma and accelerated to a defined kinetic energy. Due to its shape, the acceleration area has a focusing effect on the electron beam. The pressure in the acceleration area is less than 1 Pa. The two described pressure regimes are installed by the extraction grid which acts as pressure aperture. The system emits an electron beam with adjustable and defined energy, e.g. a 100ÂµA beam and an electron energy of 70eV. Benefits of the system are the high electron current, small dimensions (diameter of the plasma chamber is less than 1mm), the low gas and power consumption, uncritical vacuum requirements because of the small size, and the adjustable electron energy. @FootnoteText@ @footnote 1@ Plasmagestuezte Ionenquelle in Mikrosystemtechnik fuer den Einsatz in einem MMS, P.Siebert, TUHH, 2001@footnote 2@ A Micro Mass Spectrometer, G.Petzold et al. MicroTAS, 2001.

11:20am **MN-TuM10 Deep Reactive Ion Etching of Membrane-Based Devices Using a Low-Frequency Bias***, **R.J. Shul**, J. Stevens, R.P. Manginell, M.G. Blain, S.G. Rich, S.A. Zmuda, L.J. Sanchez,* Sandia National Laboratories*; M. DeVre, J. Shin, S.L. Lai,* Unaxis USA Inc.

Deep reactive ion etching (DRIE) of Si or the Bosch process is essential in the fabrication of many membrane-based devices, especially chemical and biological sensors. The process relies on the ability of the DRIE process to essentially stop on the membrane film, typically a dielectric film such as SiO@sub2@ or SiN. The ability to stop on this film is due to the high etch selectivity of Si to the membrane film. Since the SiO@sub2@ or SiN membrane is an insulator, positive charge can build up on this film upon exposure to the plasma and notching at the foot of the feature can result. The positive charge causes ions accelerated from the plasma to assume a divergent path at the Si-insulator interface and causes preferential, lateral etching of the Si at the interface, allowing a notch to form. The notch can be several microns in both the lateral and vertical dimensions and can destroy the device. Notching can be minimized and often eliminated when a low-frequency or pulsed-bias is used. In this study, we will report on the results of deep Si etching of membrane devices using a low-frequency 100 kHz bias. We will compare the results for specific device applications where both high-frequency and low-frequency biasing has been incorporated and demonstrate the relative advantages of low-frequency techniques. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

11:40am **MN-TuM11 Aspect Ratio Dependent Etching Lag Reduction in Deep Silicon Etch Processes***, **S.L. Lai**, D. Johnson, R.J. Westerman,* Unaxis USA, Inc.

MEMS device fabrications often involve 3-D structures with high aspect ratios. Moreover, MEMS designs require structures with different dimensions and ARs to co-exist on a single microchip. There is a well-documented aspect ratio dependent etching (ARDE) effect in deep silicon etching (DSE) processes. The ARDE effect can be manifested in two ways: firstly, the etch rate decreases as the aspect ratio increases for a specific feature; secondly, for features with different dimensions etched simultaneously, bigger features are etched at faster rates. For example, when a 2.5 µm-wide trench is etched simultaneously with a 100 µm-wide trench in a conventional DSE process, the resultant trench depth of the latter can be more than double that of the 2.5 µm-wide trench. Indeed, the ARDE effect causes many undesired complications to MEMS device fabrication. One of the approaches to cope with ARDE is to employ etch stop layers, such as oxide, to compensate the lag. However, disadvantages, such as notching at the silicon/oxide interface, emerges sometimes when an etch stop layer is used. At Unaxis, we have developed a proprietary technique to eliminate the ARDE effect encountered in DSE processes. Our novel technique is based on a new physical model for ARDE lag reduction. This paper presents the theoretical model and the experimental results on ARDE reduction. With controls over the passivation and etch steps employed in a TDM etch process, we have demonstrated that normal ARDE can be changed to inverse ARDE, while maintaining good etch profile in all features. DSE processes can be optimized such that ARDE is completely eliminated. In the experiments, the ARDE lag was reduced to below 3% for trenches with widths ranging from 2.5 to 100 µm; for trenches with widths ranging from 4 to 30 µm, the ARDE lag was below 2%. Such results were achieved at etch rate exceeding 2 µm/min.

Nanometer-Scale Science and Technology
Room 210 - Session NS+EM-TuM
Nanoscale Electronic Devices & Detection

Moderator: P. Grutter, McGill University

8:20am **NS+EM-TuM1 Single Electron Spin Detection in Si-Based Semiconductor Structures***, **H.W. Jiang**,* UCLA **INVITED**

Several schemes for electron spin based qubit in compound semiconductor structures have been proposed recently for quantum information processing. In order to physically implement any of the proposals, it is essential to measure the state of a single spin. Towards this end, we have done a sequence of measurements to probe the spin state of a single paramagnetic spin center adjacent to a sub-micrometer silicon metal-oxide-semiconductor field-effect transistor. Stochastic switching between two discrete values of channel current, known as random telegraph signal (RTS), has been used as a tool to sense the single spin. Magnetic-field-induced Zeeman splitting of the single spin center was measured. Using microwave radiation, we have observed that the statistical distribution between the two states changes when the electron spin resonance condition is matched. Experiments with a series of pulsed gate voltages showed promise of using the field effect transistor channel for single-shot spin state read-out. Our ongoing effort of single spin measurements in electrostatic quantum dots in a Si/SiGe 2D electron gas will be described.

9:00am **NS+EM-TuM3 Few Electron SiGe Quantum Dots***, **L.J. Klein**, S. Goswami, K.A. Slinker, S.N. Coppersmith, D. Savage, M.G. Lagally, M.A. Eriksson,* University of Wisconsin

Spins in silicon quantum dots are promising qubits for quantum information processing. Here we present an approach to combine trenchline and metal gates to fabricate quantum dots in modulation doped Si/SiGe heterostructures. Electron-beam lithography and reactive ion etching are used to define single and tunnel coupled double dots. Both Schottky and in-plane two-dimensional electron gas gates are used. Transport measurements at 0.2 K for the single and tunnel coupled double dots show Coulomb blockade with single electron charging. For the double quantum dots a transition from a single to split peaks are observed as voltages applied to the gates became more negative. A transition is observed from a large single dot to two tunnel coupled quantum dot with a well defined tunnel coupling between pairs of quantum dots. The tunnel coupling between the dots is determined by the width of the channel between the dots. To achieve a higher control of the tunnel coupling between the dots we integrate metal gates on the top of the channel in addition to side gates. The fabricated quantum structures are stable over long periods of time with minimal charge noise fluctuations. We also discuss progress towards the achievement of few electron dots using both etched and Schottky gates for electrostatic confinement.

9:20am **NS+EM-TuM4 Top-gated Quantum Dots in Silicon / Silicon-Germanium Two-Dimensional Electron Gases*, K.A. Slinker,* *L. McGuire, K.L.M. Lewis, C.C. Haselby, S. Goswami, L.J. Klein,* University of Wisconsin - Madison*; J.O. Chu,* IBM Research Division, T. J. Watson Center*; M. Friesen, M.A. Eriksson,* University of Wisconsin - Madison

Electrons in silicon/silicon-germanium two-dimensional electron gas (2DEG) quantum dots are a promising architecture for spin based quantum computation. Schottky gated quantum dots allow precise tuning of electron shape and interdot coupling; however, up until now top gates on Si/SiGe heterostructures have not been used to deplete into the tunneling regime, most likely due to problems with gate leakage. We have overcome these problems by reducing the active 2DEG area into sub-micron mesas and back gating the 2DEG to tune the carrier concentration to be depleted by the top gates. We report on the depletion characteristics of these Schottky gates as well as successful Si/SiGe quantum dot architectures incorporating top gates. For one quantum dot device, an 800 nm channel is fabricated by electron beam lithography and subsequent reactive ion etching. Metal gates are deposited across the channel to define the leads of the dot, and an etch-defined side gate is used to vary the potential in the dot. The sides of dot are defined by surface depletion from the etched sidewalls. In another device, six metal gates are used to electrostatically define the dot on all sides - a set of pincher gates on each lead and two plunger gates. Properties of the dots are presented and compared.

9:40am **NS+EM-TuM5 Spin Physics in Few-Electron Quantum Dots*, L. Kouwenhoven,*** Delft University of Technology, The Netherlands **INVITED**

Few-electron quantum dots are realized in various semiconductor materials. The conventional system for transport studies is an AlGaAs/GaAs heterostructure in which quantum dots are defined by surface gates. We have studied the spin states in one and two-electron dots. The spin states are resolved in a magnetic field that splits the one-electron spin states and also the triplet states for two electrons. We manipulate the spin states using a pulse technique that allows to determine the spin of individual electrons. As a spin off we measure the spin relaxation times under various circumstances (e.g. magnetic field). The obtained time scales are in good agreement with theory based on spin-orbit and hyperfine interaction. A new class of materials are semiconductor nanowires. We have fabricated quantum dot devices in InP and InAs wires with diameters around 50 nm. We observe discrete states and resolve Zeeman splitting of the spin states in a magnetic field. In addition we have used superconducting contacts to bias the nanowires with supercurrents.

10:20am **NS+EM-TuM7 Single Spin Detection Using Magnetic Resonance Force Microscopy*, H.J. Mamin,*** IBM Research Division*; R. Budakian,* University of Illinois at Urbana-Champaign*; B.W. Chui, D. Rugar,* IBM Research Division **INVITED**

Magnetic resonance force microscopy (MRFM) has been proposed as a method for greatly improving the sensitivity and spatial resolution of magnetic resonance imaging, perhaps even to the atomic level. In this talk, I describe recent experiments at IBM that demonstrate an important step toward this goal, namely the detection of an individual subsurface electron spin. In this technique, the spin is detected via the attonewton-scale force it exerts on a 150-nm sized magnetic tip that is attached to the end of an ultrasensitive micromachined cantilever. The spin, which is associated with a dangling bond in silicon dioxide, is manipulated by cantilever-driven cyclic adiabatic inversion, which results in a slight frequency shift of the cantilever. With this method, we were able to unambiguously detect a single spin located more than 100 nm below the magnetic tip of the cantilever and obtain a spatial resolution of 25 nm in one dimension. I will also describe recent experiments on relatively small ensembles of nuclear spins, and discuss the challenges of pushing the technique toward single nuclear spin detection. This work was supported by the DARPA-QUIST program administered through the Army Research Office.

11:00am **NS+EM-TuM9 Fabrication and Characterization of Nanolayered Electron Emitters*, A.A. Dixit,*** *A. Raigoza, T. Engstrom, A. Lapicki, K. Akutsu, D.C. Jacobs,* University of Notre Dame

Nanolayered electron emitters (vertical dimension ~ 100 nm), based on a Metal-Insulator-Metal (MIM) architecture, are fabricated by sequential deposition of thin films. A combinatorial approach is employed to efficiently screen different materials and fabrication conditions, and an array of 24 devices is fabricated in each batch. The electrical performance of each device is characterized as a function of the voltage bias applied across the metal electrodes. The total vacuum emission of electrons exhibits a non-linear increase as a function of the applied voltage bias. The kinetic energy distribution of emitted electrons is recorded at a series of bias voltages by a hemispherical energy analyzer. The energy distribution is quasiballastic with minimal inelastic losses. A change in the applied voltage bias results in a corresponding linear shift in the position of the peak in the energy distribution. The role of defects on the electron transport mechanism is discussed.

11:20am **NS+EM-TuM10 Low Temperature Scanning Tunneling Spectroscopy on Cleaved InAs Quantum Dots*, A. Urbieta,*** IEMN, (CNRS, UMR 8520) France, France*; B. Grandidier, J.P. Nys, D. Deresmes, D. Stiévenard,* IEMN, (CNRS, UMR 8520) France*; Y.M. Niquet,* CEA/DRFMC/SP2M, France

InAs quantum dots (QDs) have attracted increasing attention in recent years due to their application in optoelectronic devices such as infrared solid state lasers.@footnote 1@ Therefore, a complete knowledge of the electronic structure of the mentioned dots is essential in order to improve device design, performance and reliability. QDs are zero-dimensional structures also known as artificial atoms since they exhibit three dimensional confinement leading to atomic-like electronic states. Much effort has been devoted in the last decade to determine the characteristics of these states from both theoretical and experimental viewpoints. The spectroscopic mode of scanning tunneling microscope (STM) at cryogenic temperatures is a powerful tool to study low dimesional structures, since it enables a detailed characterization of their local electronic properties with high resolution. Actually, electron states in free-standing InAs QDs grown on n-type GaAs have been successfully investigated using this technique.@footnote 2@ However, a complete characterization of QD-related hole states is still lacking. In this work, scanning tunneling spectroscopy at low temperatures has been used to investigate the electronic structure of cleaved InAs quantum dots growth on p-type (001) GaAs. Several peaks related to energy levels of electrons and holes confined in the dots have been observed. The experimental results are compared with tight-binding calculations of the electronic structure of similar quantum dots, which allow us to determine both the ground state and first excited states of electrons and holes. Wave function mappings have been also carried out in order to assess the symmetry of the QDs states. @FootnoteText@ @footnote 1@ Y. Qiu, P. Gogna, S. Forouhar, A. Stintz and L. F. Lester, Appl. Phys. Lett. 79, 3570 (2001).@footnote 2@ T. Maltezopoulus, A. Bolz, C. Meyer, C. Heyn. W. Hansen, M. Morgenstern and R. Wiesendanger, Phys. Rev. Lett. 91, 196804 (2003).

11:40am **NS+EM-TuM11 Nanometer Spaced Electrodes on Ultra Flat GaAs-AlGaAs Heterostructures for Molecular Electronics Applications*, S.M. Luber,*** *F. Zhang, S. Strobel, A. Hansen,* Walter Schottky Institut, TU Muenchen, Germany*; D. Schuh,* Universitaet Regensburg, Germany*; M. Bichler, M. Tornow,* Walter Schottky Institut, TU Muenchen, Germany

Current efforts in molecular electronics both aim for novel devices as well as the fundamental understanding of the electronic transport in molecular "wires". Here one of the major challenges is the preparation of well defined electrodes which allow reliably contacting and electrically investigating molecules of a given size. We pursue a novel strategy to fabricate nanometer spaced (nanogap) metal electrodes which is based on a cleavage plane of a GaAs-AlGaAs heterostructure. This allows for a precisely predetermined spacing of the electrodes. In recent studies@footnote 1@ we successfully fabricated, characterized and verified the electrical functionality of such nanogap electrodes. Using Molecular Beam Epitaxy (MBE) we embedded a thin (5-20nm) GaAs layer in between two AlGaAs layers. By cleaving the substrate and selectively etching the GaAs layer, the remaining AlGaAs layers are used as a support for deposited metal (Au) electrodes. This device is especially useful for measuring plenty of nanoscale objects in parallel, as the lateral size of the electrodes is defined by optical lithography. In our contribution we will report on a) first electrical investigations on thiolated @pi@-conjugated aromatic molecules assembled on 5nm spaced electrodes, and b) on our recent progress to reduce the lateral electrode size to a few nanometers only. Such electrode shape will allow for the contacting of merely a few or even single nanoscale objects. The downsizing is possible by the insertion of a second MBE growth step perpendicular to the first growth direction using the Cleaved Edge Overgrowth (CEO) technique. We successfully fabricated metallized electrodes of various widths (5-50nm) and various distance (15-30nm). We investigated these electrodes by AFM and SEM and made a first electrical characterization. @FootnoteText@ @footnote 1@SM Luber, S Strobel, HP Tranitz, W Wegscheider, D Schuh, and M Tornow, Nanotechnology 16 (2005), in press.

Plasma Science and Technology
Room 302 - Session PS+BI-TuM

Plasmas in Bioscience

Moderator: P. Favia, University of Bari, IMIP-CNR, Plasma Solution Srl, Italy

8:20am **PS+BI-TuM1 Plasma Polymerisation of Ethanethiol***, **S.L. McArthur**, G. Mishra, A.G. Shard,* University of Sheffield, UK

The past years have seen significant development and use of functional polymer surfaces for bio-medical applications. Plasma polymerisation has proved to be one technique to generate functional surface in a single step process. Spontaneously reactive thiol surfaces produced by various wet chemistry routes have been extensively characterised as models to study surface-ligand interactions. This project aims to develop thiol functionalized surfaces utilizing plasma polymerisation of ethanethiol and with 1, 7 Octadiene as a diluent monomer. The deposited film properties were determined by X-Ray photoelectron spectroscopy and a fluorine marker was used to label any functional thiol groups present. It was observed that plasma polymerisation of ethanethiol at low discharge power resulted in a sulphur rich stable coatings and by increasing the power the coating resembled monomer composition in terms of atomic percentages, but none of the used conditions generated any detectable thiol groups. Mixing 1-7 Octadiene in a ratio of 1:1(v/v) in the gaseous feed resulted in an interesting change at high powers in the film properties with generation of 3-4% detectable active thiol groups without affecting the stability of the film. It is believed that the introduction of a diluent monomer at high powers has reduced the amount of available sulphur for crosslinking which dominates the deposition mechanism at low powers and has created a reaction pathway which favours the generation of thiol groups at the surfaces.

8:40am **PS+BI-TuM2 A Novel, Single-Step Method for the Preparation of Chemical Gradient Surfaces Using Non-Uniform Plasma-Deposition***, **T.R. Gengenbach**, P.G. Hartley, H. Thissen, K.M. McLean, L. Meagher, G. Johnson,* CSIRO Molecular Science, Australia

Gradient surfaces are characterised by a gradual and systematic variation of one or more chemical and physical properties along a specific direction. They are of increasing importance in combinatorial chemistry and materials science where they are being used to generate libraries of widely varying surface properties to study interfacial phenomena. In biomaterials research gradient surfaces can be employed to rapidly explore multi-variable parameter space, either to investigate how relevant variables (e.g. surface chemistry, wettability, charge) affect biocompatibility, or alternatively, to accelerate the optimisation of coupling strategies for covalent attachment of secondary layers. Radio frequency glow discharge plasma polymer coatings form robust thin films which contour and adhere strongly to the surfaces of polymeric and other materials. Their ability to modify surface properties, either by enhancing biocompatibility, or by introducing defined chemical functionalities at interfaces for the subsequent coupling of bioactive molecules, have seen their widespread application in the field of biomaterials research. We have developed a novel method to deposit plasma polymer coatings with systematically varying properties along the surface. In a standard plasma reactor with capacitively coupled electrodes the substrate to be coated is placed on a large flat horizontal base electrode (earthed); the second, specially shaped top electrode (active) is lowered to within millimetres of the substrate surface. The resulting plasma discharge is spatially non-uniform and produces surfaces with a strong gradient of chemical/physical properties. By controlling the shape of the top electrode we have also prepared patterned surfaces with well defined regions of widely different properties (e.g. density of specific functional groups). These gradient surfaces have been evaluated with respect to the biological response, such as protein adsorption and cell attachment.

9:00am **PS+BI-TuM3 Mechanistic Musings on Plasma-Enhanced CVD of Polymeric Materials***, **E.R. Fisher**,* Colorado State University **INVITED**

Plasma-enhanced chemical vapor deposition (PECVD) is a valuable technique for deposition of polymeric materials with wide ranging applications, including micropatterns for fabrication of multianalyte biosensors, diagnostic tests, DNA microchips, and genomic arrays. One ongoing issue with PECVD processes is controlling and tailoring the molecular level chemistry, both in the gas-phase and at the gas-surface interface such that predictable and reproducible film chemistries can be created. One method for controlling the overall deposition is to use pulsed, downstream or remote deposition processes. Moreover, understanding surface interactions of plasma species provides critical molecular level information about PECVD processes. The imaging of radicals interacting with surfaces (IRIS) technique examines interactions of radicals during plasma deposition using laser-induced fluorescence (LIF) to provide spatially-resolved 2D images of radical species involved in film formation. IRIS allows for direct determination of radical-surface interactions during plasma processing. IRIS data for species in plasma polymerization and plasma modification systems will be presented, along with addition film and gas-phase composition data. IRIS results that will be discussed include data on fluorocarbon radicals (CF and CF@sub 2@), main group hydrides (SiH, OH, NH, and CH), and nitrogen-containing molecules (NH, NH@sub 2@, CN) in relationship to various plasma polymerization systems of interest to the microelectronics and coating industries. Correlation of gas-phase data, surface analysis, and plasma-surface interface reactions will also be presented to provide more comprehensive mechanisms for overall plasma polymerization processes. Examples will also be provided from polymer film and fiber modification systems.

9:40am **PS+BI-TuM5 Application of Plasma Discharges in the Biomedical Field: Biological Decontamination and Sterilization of Surfaces***, **F. Rossi**,* European Commission-Joint Research Centre, Italy **INVITED**

Every year, thousands of patients die from nosocomial infections got in hospital after surgical intervention. Those infections are directly linked to bacterial contamination of medical devices surfaces that are used during operation. Moreover, interaction of specific biomolecules like phospholipids or lipopolysaccharides (LPS) or certain proteins with organisms can be a major cause of diseases. Prominent examples are pyrogenes - lipopolysacharides (LPS) and lipoteichoic acids (LTA) -, which cause fever in human body and are potentially lethal after contact with blood. In some cases the secondary or tertiary structure of proteins is responsible for their biological properties. Important example is PrP (prion) which becomes pathogenic after a change of its structure. The contaminated surface (e.g. medical devices, accessories, work surface or tissue) cannot be decontaminated with current sterilisation practices without inducing major damage to the substrate or tissue itself, because of the high temperature used, or chemical reaction with the surface. In the present work, the inactivation or modification of biologically potentially harmful molecules is addressed in a combined approach using low pressure plasma discharges with non toxic gas mixtures. The emerging species fluxes of these plasmas are measured. Different characteristic biomolecules (LPS, LTA, proteins etc. as well as whole micro-organism cells) are exposed to the plasmas and the changes induced are monitored in-situ using infrared spectroscopy as well as ex-situ using biochemical and structural analysis as a function of the gas mixture and plasma parameters. Different potential mechanisms (etching, UV radiation, chemical reactions) are presented. The gained knowledge on the interaction of plasma discharges with pathogenic biomolecules and microorganisms allows a targeted development of decontamination strategies for very resistant species. The potential applications are in the field of surface decontamination and sterilisation of medical objects and opens large possibilities of applications in the field of security.

10:20am **PS+BI-TuM7 Biological Response to Plasma Processed Materials***, **L.C. Lopez**,* University of Bari, Italy*; R. Gristina,* CNR-IMIP Bari, Italy*; L. Detomaso, P. Favia, R. d'Agostino,* University of Bari, Italy **INVITED**

The demand of biomedical implants significantly increases every year and several approaches have been investigated to develop surfaces which are recognized by specific proteins of the biological milieu, ranging from template materials, to surfaces that mimic receptor sites, to biologically inspired materials. Other surface modifications approaches deal, instead, with the immobilization of biomolecules (heparine, carbohydrates, peptides, enzymes, etc.) on biomedical surfaces, to induce the growth of cells, to act as sensors in immunodiagnostics or to exhibit blood compatibility. Low temperature plasma modification processes represent an appealing tool, versatile and environmental friendly, to selectively modify materials to be used for medical devices. Surface properties of biomaterials (chemical, biological, tribological) can be selectively plasma driven to achieve specific biological response, leaving the bulk features unaltered.@footnote 1@ Furthermore, a promising strategy to control the interaction between biomaterials and biological environments, applies to binding of biomolecules to plasma modified polymers by a stable bond with surface functional groups (OH, COOH, NH@sub2@, etc.).@footnote 2@ RGD-containing peptides and galactose immobilization on plasma processed substrates, recently investigated in our group, clearly highlighted a strict correlation between specific cellular behaviour and immobilised molecules. These results plainly indicate that coupling plasma modification processes with precise biomolecules immobilization pathways may represent a successful approach to address biocompatibility and biorecognition requirements of biomaterials. @FootnoteText@ @footnote 1@ B.D. Ratner in: Plasma Processing of Polymers, R. d'Agostino, P. Favia, F. Fracassi ed., Kluwer Acad. Publ., NATO ASI Series, E: Appl. Sci., Vol. 346, 1997.@footnote 2@ L. C. Lopez, R. Gristina, G. Ceccone, F. Rossi, P. Favia, R. d'Agostino Surface and Coatings Technology, 2005, in press.

Plasma Science and Technology
Room 304 - Session PS-TuM

Plasma Surface Interactions I

Moderator: E.C. Benck, National Institute of Standards and Technology

8:20am **PS-TuM1 Investigation of Plasma-Surface Interaction by Sheath-Lens Focusing Effects***, **E. Stamate**, H. Sugai,* Nagoya University, Japan

Present trends in nano-technologies involve reactive plasmas of complex chemistry that makes it difficult to evaluate and control all surface reactions. Recently we discovered that the sheath forming to a biased target interfacing an insulator acts as an electrostatic lens that exhibits two focusing effects.@footnote 1@ The discrete-focusing leaded to the formation of a passive surface of no charge impact, near the target edge, and the modal-focusing resulted in the formation of certain modal-spots and/or modal-lines on the active surface. So far, several applications to plasma diagnostics (negative ion detection, sheath thickness measurements) and ion flux control in plasma immersed ion implantation have been reported. In this work we are demonstrating by simulations and experiments the possibility to use the focusing effects to investigate the surface reactions induced by beams of focused positive and negative ions and/or dusty particles. Measurements are done in DC and ICP discharges using Ar/SF6, O2 and CF4 gases. Sheath accelerated ion beams with energy ranging from 50 to 500 eV are directed by focusing effect to samples of various geometries (disk, square and complex three-dimensional shapes) made of different materials (metals or semiconductors). Surface investigation by AFM and SEM shows the influence of the ion dose and incidence angle to the sputtered profile. Depending on the competition between sputtering and deposition of by products the formation of cluster like structures is also observed. Simulations of the sheath potential structure and ion and dust kinetics are done in three dimension. The ion and dust flux on target surface is found in an excellent agreement with experiments. This work was partialy supported by the 21st Century COE Program of MEXT, Japan. @FootnoteText@@footnote 1@ E. Stamate and H. Sugai, Phys. Rev. Lett. 94, 125004 (2005).

8:40am **PS-TuM2 Effects of Polymer Deposition on Density Stabilization and Loss Rate of Radical Species in Fluorocarbon Plasmas***, **K. Kumagai**, K. Nakamura,* Chubu University, Japan*; K. Oshima, T. Tatsumi,* Sony, Japan

Fluorocarbon discharges have been widely used for etching processes of dielectric thin films for microfabrication. However, these have suffered from various problems, in particular, repeatability of the etching characteristics. The problem becomes recently severe due to narrow process margin for next generation ULSI devices. One of the major origins is plasma-surface interaction on polymer-deposited vessel wall, leading to significant time-variation of radical composition of the plasma. Alternating ion bombardment (AIB) method has been proposed to reduce such interactions by applying an RF bias to the chamber wall.@footnote 1@ We reports on the effects of polymer deposition on the density variation and loss rate of radical species in fluorocarbon plasma reactors. 13.56 MHz inductively-coupled plasmas were produced in Ar-diluted C@sub 4@F@sub 8@ gases in a stainless steel chamber in which two semi-cylindrical electrodes are set. A 400 kHz RF source serves alternating negative bias to the electrodes, and the AIB could control the deposition rate of the polymer on the biased wall. The radical density reached a steady state more quickly when the polymer deposition was suppressed with the AIB. In order to investigate the mechanism, as a parameter of thickness of the polymer, we measured a decay time of the radical density immediately after only the bias was turned off keeping the plasma-existing conditions. The delay time corresponding to a loss rate of the radical species increased with an increase in the polymer thickness, suggesting that the polymer deposition affected the loss rate. To keep the polymer thickness will be crucial for stabilization of the radical density. @FootnoteText@ @footnote 1@K. Nakamura et al: J. Vac. Sci. Techonol. A 18 (2000) 137.

9:00am **PS-TuM3 Angular Dependence of Si@sub 3@N@sub 4@ Etch Rates and the Etch Selectivity of SiO@sub 2@ to Si@sub 3@N@sub 4@ at Different Bias Voltages in a High Density C@sub 4@F@sub 8@ Plasma***, J.-**K. Lee**, J.-H. Min, S.H. Moon,* Seoul National University, South Korea

The dependence of Si@sub 3@N@sub 4@ etch rates and the etch selectivity of SiO@sub 2@ to Si@sub 3@N@sub 4@ on the ion-incident angle was studied at different bias voltages in a high density C@sub 4@F@sub 8@ plasma. A Faraday cage and specially designed substrate holders were used to accurately control the angle of ions incident on the substrate surface. The normalized etch yield (NEY), defined as the etch yield normalized to one obtained on a horizontal surface, was unaffected by the bias voltage in Si@sub 3@N@sub 4@ etching but increased with the bias voltage in SiO@sub 2@ etching, in the range of -100 V ~ -300 V. The NEY changed characteristically, showing a maximum, with the ion-incident angle in the etching of both substrates. In Si@sub 3@N@sub 4@ etching, the maximum NEY of 1.7 was obtained at 70° in the above bias voltage range. However, the increase in the NEY with the ion-incident angle was smaller for SiO@sub 2@ than for Si@sub 3@N@sub 4@ and, consequently, the etch selectivity of SiO@sub 2@ to Si@sub 3@N@sub 4@ decreased with the ion-incident angle. The etch selectivity decreased with the ion-incident angle to smaller extents at high bias voltages because the NEY of SiO@sub 2@ was high under this condition. To understand the characteristic changes in the NEY for different substrates, we estimated the thickness of a steady-state fluorocarbon (CF@sub x@) film formed on the substrates. The thickness of a film on Si@sub 3@N@sub 4@ changed with the ion-incident angle, showing a minimum at 70°, and the film thickness was reduced at high angles to smaller extents on SiO@sub 2@ than on Si@sub 3@N@sub 4@. These results indicate that the NEY can be correlated with the thickness of a steady-state CF@sub x@ film formed on the substrate surfaces.

9:20am **PS-TuM4 Fluorocarbon Film Deposition in a Gap Structure and Correlation With Trench Sidewall Angle for Fluorocarbon Chemistries in Capacitively Coupled Discharges***, **L. Ling**, X. Hua, B. Orf, G.S. Oehrlein,* University of Maryland at College Park*; E.A. Hudson,* Lam Research Corp.*; P. Jiang,* Texas Instruments*; Y. Wang,* National Institute of Standards and Technology

A small gap structure* has been used to study surface chemistry aspects of fluorocarbon (FC) film deposition for FC plasmas produced in a mechanically confined dual-frequency capacitively coupled plasma (CCP) reactor. The small gap structure provides a completely shadowed region without direct ion bombardment, similar to surfaces of sidewalls of trench patterns. On both trench sidewalls and the shadowed surface portions of the small gap structure, very thin fluorocarbon layers are formed by neutral diffusion. The lack of ion bombardment also increases the retention of the chemical structure of the FC film precursors in the deposited films. For C@sub 4@F@sub 8@/Ar, C@sub 4@F@sub 8@/Ar/O@sub 2@ and C@sub 4@F@sub 8@/Ar/N@sub 2@ discharges the deposition rate, composition, and bonding of deposited FC films are determined as a function of processing conditions using ellipsometry and X-ray photoemission spectroscopy. The deposition rate and surface chemistry of FC film deposited in this region depend strongly on discharge chemistry, and atomic force microscopy shows significant nanoscale topography that differs markedly from films produced with simultaneous ion bombardment. The inclinations of feature sidewalls formed for different conditions qualitatively correlate with the deposition rates measured for shadowed surfaces of the gap structure. Results of mass spectrometric investigations are also reported in an attempt to relate the observed compositional differences to radicals produced in the gas phase. @FootnoteText@ * L. Zheng, L. Ling, X. Hua, G. S. Oehrlein, and E. A. Hudson, J. Vac. Sci. Technol. A 23, xxx (2005).

9:40am **PS-TuM5 The Spontaneous Etching of Silicon by F Atoms, Cl Atoms and XeF@sub 2@ : A Unified Model Supported by Experiment and Simulation*, H. Winters,*** University of California at Berkeley*; D. Humbird, D.B. Graves,* University of California, Berkeley **INVITED**

Insights gained from a recent molecular dynamics simulation (denoted HG) are used to refine a model that quantitatively predicts spontaneous etch rates of silicon and explains various experimental observations@footnote 1@ This model is based on the electronic structure of Si and the electron affinity of the incident gas, and assumes that the rate-limiting reaction step is associated with negatively-charged particles in the halogenated Si surface layer. The density of such charge centers in the layer is a function of its thickness and can be calculated using a formalism similar to one previously published.@footnote 2@ HG predicts a ~5 @Ao@-thick SiF@sub x@ layer on undoped silicon exposed to F atoms; XPS data agree with this prediction, and indicate that the layer is about twice as thick for XeF@sub 2 @exposure. Layer thickness is observed via XPS and temperature programmed desorption to be independent of incident halogen flux and temperature over significant ranges of these parameters, also consistent with the HG simulations. Closed-form expressions for the reaction probability of Si (111) as a function of various parameters will be presented. These expressions correlate well with experiments, including reaction probability measurements as a function of temperature (200K--1000 K), dopant concentration (~10@super 15 @ - 10@super 20@ dopants/cm@super 3@), and incident species (F, Cl, and XeF@sub 2@). The model rationalizes the observation that the doping effect in Cl is large relative to F, even though the opposite trend is observed for the spontaneous etch rate. Finally, the HG result that etch products desorb with significant kinetic energy allows modulated beam mass spectrometry data to be quantitatively calibrated, making measured etch reaction probabilities absolute. @FootnoteText@@footnote 1@ D. Humbird and D. Graves, J. Appl. Phys. 96 791 (2004) @footnotes 2@ H.F. Winters and D. Haarer, Phys. Rev. B 36 6613 (1987) See also erratum @footnote 3@ H.F. Winters and D. Haarer, Phys. Rev. B 36 6613 (1987)

10:20am **PS-TuM7 Molecular Dynamics Simulations of Ar@super +@ Bombardment of Si: Characterizing Ion-Induced Disorder at Surfaces*, D. Humbird,*** Lam Research Corporation*; D.B. Graves,* University of California at Berkeley*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands

Previous molecular dynamics (MD) simulations of energetic Ar@super +@ ions bombarding initially crystalline Si surfaces indicated the formation of an amorphous phase of Si on top of crystalline Si. This amorphous phase is established within 1 monolayer of Ar@super +@ fluence, and under continuous bombardment it reaches a steady-state thickness that is a function of the impacting ion energy. We revisit some of these calculations with a different potential energy function that predicts the same general behavior, but also permits accurate simulation of F atoms interacting with a Si surface. We discuss changes to the average Si-Si bond length, bond angle, and other local order parameters as a result of Ar@super +@-induced amorphization. We note sharp transitions of these properties at the interface between amorphous and crystalline Si. Finally, we discuss differences in uptake and etch rate when thermal F atoms adsorb on and spontaneously etch the amorphous and crystalline surfaces. Some parallels are drawn between the simulations and recent real-time ellipsometry and second harmonic generation experiments, which give information on amorphous layer formation, and on bond disorder at the interface and surface of the amorphous layer, respectively.

10:40am **PS-TuM8 Fluorocarbon Polymer Layers and Etching: the Role of Fluctuations, Cluster Ejection, and Redeposition*, J.J. Vegh*[1]*,*** *D. Humbird, D.B. Graves,* University of California, Berkeley

Fluorocarbon (FC) plasma etching is known to result in the formation of a FC-containing 'polymer' film during etch, but the nature of this film remains poorly understood. Understanding and control of this film are essential to meet goals for etch of novel materials (e.g. ultra low-k (ULK) dielectrics) and to minimize photoresist loss and surface roughening during FC plasma etch. Molecular dynamics (MD) simulations of Si etch with FC radicals, F atoms, and argon ions suggest that local film thickness fluctuations are common. These fluctuations result from ejection of clusters of FC (~C@sub 20@F@sub 20@) by Ar@super +@ impacts. Temporary, local thinning of the FC film by cluster removal allows subsequent Ar@super +@ impacts to penetrate into the underlying substrate and facilitate Si etch through the deposition of kinetic energy. Similarly, transport of F atoms to the underlying Si and of etch products to the vacuum are both facilitated by this mechanism. These phenomena have been observed in simulation previously, but the relationships between cluster removal and the formation and persistence at steady state of the fluctuating FC film are not yet clear. This fluctuation effect has not been reported experimentally, to our knowledge. We have collected statistics on the FC clusters formed during etching simulations. We report the relationship between cluster size and composition to various local and instantaneous properties in the near-surface region. These properties include the average FC film thickness and Si etch yield; fluctuations in FC film thickness and surface coverage; incident FC species type and energy; density of the FC film, and incident Ar@super +@ energy. We have simulated cluster re-deposition as well. We conclude that film fluctuation through cluster ejection and perhaps redeposition of clusters play an integral role in the maintenance of the FC overlayer.

11:00am **PS-TuM9 Molecular Dynamics Investigation of the Etching of Passivated SiOCH Low-@kappa@ Dielectric Films*, V. Smirnov,*** *A. Stengatch, K. Gainullin, V. Pavlovsky,* SarovLabs, Russia*; S. Rauf, P. Ventzek,* Freescale Semiconductor, Inc.

Fluorocarbon plasmas are widely used for etching of dielectric thin films (conventional and low-@kappa@) in the microelectronics industry. Fluorocarbon radicals and ions are known to produce a nanometer-scale passivation layer on the dielectric surface, whereupon energetic ion bombardment leads to dielectric material etching. As the passivation films are extremely thin and in-situ monitoring is difficult during etching, very few experimental studies have been able to probe into the fundamental nature of fluorocarbon based etching of low-@kappa@ dielectrics. This paper reports about a computational molecular dynamics (MD) investigation of the etching of SiOCH low-@kappa@ dielectric films by CF@sub x@@super +@ (x=1, 2, 3), SiF@sub x@@super +@ (x=1, 2, 3), CHF@sub x@@super +@ (x=1, 2), and Ar@super +@ ions. The MD model is 3-dimensional and uses the velocity-Verlet method for particle acceleration. Psudo-potentials for two and three body interactions of Si, O, C, H, F, and Ar have been assembled either using Gaussian based quantum chemistry computations or data available in the literature. The test structures for the MD studies are prepared by starting with crystalline Si and depositing mixtures of SiO@sub x@@super +@, CH@sub x@@super +@ and H@super +@ ions. Film stoichiometry and density can be controlled by means of ion fluxes and energies. A passivation layer is grown on the low-@kappa@ test structures through low energy fluorocarbon ion bombardment. Impact of energetic (100-300 eV) ions on passivated dielectric films is investigated in this paper, and modeling results are used to determine ion etching yields, nature of sputtered clusters, and their energy and angular distributions.

11:20am **PS-TuM10 Scattering Dynamics of Energetic F@super +@ Ions on Si and Al Surfaces*, J. Mace,*** *M.J. Gordon, K.P. Giapis,* California Institute of Technology

Fluorine is a significant component of many processing plasmas. Its reactions with surfaces have been extensively studied in the presence and/or absence of ion bombardment. Yet, little is known about the interaction of energetic F@super +@ ions with fluorinated semiconductor and metal surfaces, perhaps because of the difficulty in conducting well-defined experiments with F@super +@ beams. Using high flux (monolayers/sec) of F@super +@ extracted from an inductively-coupled plasma (ICP) source coupled to a mass-selective beamline accelerator, we have studied the scattering dynamics of 50-1000eV tunable F@super +@ ion beams with Si and Al surfaces. Energy and mass analysis of all scattered products was performed by a triply-differentially pumped electrostatic energy analyzer preceeding a quadrupole mass spectrometer capable of detecting single ions. We observed a transition from elastic to inelastic behavior at 500 and 300eV for Si and Al, respectively, where the directly scattered F@super +@ exits the surface with energy considerably lower than that predicted from binary collision theory due to quantum mechanical effects. At the threshold energy, we observed the onset of F@super ++@ production at considerably lower energy than F@super +@. The inelastic energy losses were attributed to formation of doubly-excited auto-ionizing states of F and F@super +@. In addition, we also saw in much greater yield low-energy (5-20eV) scattered F@super +@, believed to be generated via a stimulated desorption process involving charge transfer to the incident ion from an F atom bound to the surface, leaving the latter in a highly repulsive state. We have also monitored all scattered ionic products as a function of beam energy and identified SiF@super +@ as the dominant fluorinated species emitted from a Si surface, while SiF@sub 2@@super +@ was barely detectable. The implications of these findings for plasma etching and profile evolution will be discussed in the talk.

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[1] **PSTD Coburn-Winters Student Award Finalist**

11:40am **PS-TuM11 IRIS Studies of SiCl@sub x@ Surface Interactions in SiCl@sub 4@ Plasmas*, I.T. Martin,*** *D. Liu, E.R. Fisher,* Colorado State University

Chlorine based plasmas, such as SiCl@sub 4@, are widely used for Si etch processes. Additionally, SiCl@sub 4@/H@sub 2@ plasmas are utilized to deposit a-Si materials. We have characterized SiCl@sub 4@-based plasma systems using LIF, OES, and MS measurements. Density measurements indicate that relative SiCl@sub 2@ densities strongly rely on plasma parameters such as power and pressure. We have used our imaging of radicals interacting with surfaces (IRIS) method to measure the surface interactions of SiCl@sub 2@ radicals with Si substrates in SiCl@sub 4@-based etch and deposition systems. Preliminary data show significant SiCl@sub 2@ surface production (S(SiCl@sub 2@)>2) in all etch systems. These results will be compared to SiF@sub 2@ and CF@sub 2@ IRIS data, as these molecules are isoelectronic to SiCl@sub 2@. Our results indicate all three molecules behave similarly under etching conditions. Surface interaction data from power, pressure and feed-gas ratio dependence studies will be presented for both etching and deposition plasmas. SiCl@sub 2@ IRIS data will also be compared to previous experimental and theoretical work on SiCl@sub 2@ surface interactions.

Advanced Surface Engineering
Room 201 - Session SE-TuM

Hard Coatings and Wear Mechanisms of Protective Coatings

Moderator: A.A. Voevodin, Air Force Research Laboratory

8:20am **SE-TuM1 Structure and Properties of TiBN Coatings Deposited by Reactive Arc Evaporation*, J. Neidhardt,*** *C. Mitterer,* University of Leoben, Austria*; Zs. Czigány,* Research Institute for Technical Physics and Materials Science, Hungary*; M. O'Sullivan,* Plansee AG, Austria

TiBN based coating systems have been shown to have a high potential as wear protective coating owing to their outstanding mechanical properties as well as their chemical and thermal stability. However, the industrial scale synthesis has been very limited so far, presumably due to the sensitivity of the target materials and the therefore low deposition rates as well as the commonly high intrinsic stresses. This study reports, thus, on high-rate (30 - 40 nm-min@super -1@) TiBN coating deposition by reactive arc evaporation in a commercial Balzers Rapid Coating System at different N@sub 2@ partial pressures. Decreasing the bias voltage to -20V is shown to reduce the intrinsic stress and in turn to improve the adhesion on various substrates, e.g. high speed steel and (100) Si. XRD as well as high-resolution transmission electron microscopy in combination with selected area electron diffraction revealed that all coatings contain fcc crystallites, whereas the increasing lattice parameter at lower N@sub 2@ partial pressures indicates a supersaturated solid solution of B in fcc TiN. At higher N@sub 2@ partial pressures an amorphous BN phase forms, whereas its extent scales with the N@sub 2@ fraction. Nano-indentation revealed a maximum in hardness at approximately 40 GPa for the TiBN single phase solid solution which drops to 22 GPa for the coating grown in pure N@sub 2@. Ball-on-disc tests against alumina at 5N showed that the high hardness of the single phase material results in a by one order of magnitude reduced wear coefficient with respect to the coating containing the additional amorphous phase, even though the coefficient of friction remained constant at 0.7 to 0.8

9:00am **SE-TuM3 The Origin of the Hysteresis Effect in Reactive Sputtering Processes*, S. Berg*,** *T. Nyberg, O. Kappertz, T. Kubart, D. Rosen,* Uppsala University, Sweden **INVITED**

Sputtering is a well known and widely used thin film coating technique. The way the energetic incoming particle generates a collision cascade in the target that causes some of the surface atoms to be ejected is reasonable well understood. Since there is negligable consumption of the inert gas (normally argon) process control is not a problem. The sputtering process may easily be modified. By adding a reactive gas to a sputtering system it is possible to obtain a reactive sputtering process. This process, however, exhibits a significantly more complex processing behaviour than inert sputtering.The processing curves will form hysteresis loops where the processes have a tendency to make avalanche like abrupt transitions at the edges of the hysteresis width. Before the transition a metal rich film may be formed at high deposition rate while after the transition a compound film will be deposited at a low deposition rate. Without a sophisticated feedback control system no compositions in between these two extremes can be reached. Unfortunately the most attractive processing point is located at one of the critical edges of the hysteresis loop. This complicates industrial production carried out by these processes. The aim of this presentation is to describe the cause of the hysteresis loop and point out how different processing parameters will influence the hysteresis. The possibility to eliminate the hysteresis and obtain non-critical stable processing conditions will also be discussed. In addition comments will be made about common mis-information in reporting data from reactive sputtering processing experiments.

9:40am **SE-TuM5 Nanostaircases: An Atomic Shadowing Instability during Epitaxial CrN(001) Layer Growth*, D. Gall,*** Rensselaer Polytechnic Institute

Epitaxial CrN(001) layers, 57 and 230 nm thick, were grown on MgO(001) at 700 °C by ultra-high-vacuum magnetron sputter deposition in pure N@sub 2@ discharges. An oblique deposition angle @alpha@ = 80° was utilized to purposely increase the effect of atomic shadowing on surface morphological and microstructural evolution. The layers are single crystals with a surface morphology that is characterized by dendritic ridge patterns extending along orthogonal directions superposed by square shaped super mounds with edges. The ridge patterns are due to a 2D growth instability related to a gradient in the adatom density while the supermounds form due to atomic shadowing. The supermounds protrude out of the surface and capture a larger deposition flux than the surrounding layer. This leads to both vertical and lateral growth and the formation of inverted pyramids that are epitaxially embedded in a single crystalline matrix. The inverted pyramids are terminated by 1-3 nm wide tilted voids that form nanostaircases due to kinetic faceting along orthogonal {100} planes.

10:00am **SE-TuM6 The Effects of Si Additions on the Structure and Mechanical Properties of Mo-Si-C and Zr-Si-C Thin Films*, J.E. Krzanowski,*** University of New Hampshire

The effects of Si additions on the mechanical properties of molybdenum carbide and zirconium carbide thin films have been examined in this study. Mo-Si-C and Zr-Si-C thin films were deposited by magnetron co-sputter deposition using carbide targets. The films were deposited onto Si substrates at 350C for Mo-Si-C and 450C for Zr-Si-C. The structure, texture and crystallinity of the films were analyzed using x-ray diffraction, and high-resolution transmission electron microscopy was used to study film microstructure. X-ray photoelectron spectroscopy (XPS) was used to determine film composition and also to assess the chemical state of the carbon, as well as oxygen impurities, in the films. For Mo-C films with no or little Si, the structure was hexagonal; as the Si content increased, a transition to a face-centered cubic structure was observed. At the highest Si contents (10-14%) the structure was essentially amorphous. The TEM studies showed as Si was added, the grain size was reduced and confirmed the amorphous structure at the high Si contents. The texture of the films also evolved with Si content, showing oriented films at low Si but random grain structures (continuous Debye rings) at intermediate Si concentrations. The mechanical properties of the films were analyzed using nano-indentation, and showed little change in hardness over the entire range of film compositions. Zr-Si-C films were similarly studied, and showed a stronger tendency for amorphization as Si was added. The nano-indentation tests on these films showed a peak in hardness near 18% Si, where the hardness of near 30 GPa was more that 50% higher than for ZrC films alone, while the film modulus increased only slightly. Initial TEM studies show that films with added Si have a higher density, which may be a factor contributing to the observed hardness increase.

10:20am **SE-TuM7 The Effects of Water Vapor on the Friction Coefficient of Near Frictionless Carbon*, W.G. Sawyer,*** *P.L. Dickrell,* University of Florida*; A. Erdemir,* Argonne National Laboratory **INVITED**

Diamond-like carbon (DLC) films are of tribological interest due to their low friction, low wear rate, high hardness, and chemical inertness. These films can potentially be used in a wide range of applications, such as bearings, cutting tools, submersible parts, and biomedical applications. One class of diamond-like carbon coatings termed near frictionless carbon (NFC) that was developed at Argonne National Laboratory have been shown to sustain superlow coefficients of friction (μ < 0.003) and wear rates (K < 3-10 mm3/Nm) in self-mated contacts. The tribological behavior of these films is sensitive to the environment, only realizing their low coefficient of friction and wear rate in inert, dry, or vacuum environments. Using a microtribometer that is enclosed in a controlled environmental chamber the coefficient of friction over a range of surface temperatures and gaseous water vapor pressure was measured. The normal load for these experiments was 100 mN, the reciprocating speed was 18 mm/s, and the reciprocating path length was 0.6 mm. The oxygen partial pressure was measured to be less than 10 ppm for all experiments. The relative humidity varied from nominally dry to approximately 40%. The surface temperatures varied from 35C to 100C. The friction coefficient data will be presented with an accompanying uncertainty analysis. Using the friction coefficient to estimate the fractional coverage of adsorbate or percentage of effected sites, the data set was fit to an adsorption and desorption equation. This curve fitting revealed an activation energy of approximately 50 kJ/mol, which is consistent with the activation barrier for water.

11:20am **SE-TuM10 Tribological Behavior and Thermal Stability of TiC/a-C:H Nanocomposite Coatings***, **Y.T. Pei**, D. Galvan, J.Th.M. De Hosson,* University of Groningen, The Netherlands

Advanced TiC/a-C:H nanocomposite coatings have been produced via reactive deposition in a closed-field unbalanced magnetron sputtering system (Hauzer HTC-1000). These wear-resistant coatings are targeted for automotive applications where high-load bearing capacity, low friction and wear rate are the primary requirements. In this paper, the tribological behavior of the nanocomposite coatings is scrutinized by means of ball-on-disc tribo-tests in the temperature range of 20-400°C and in different environments, in conjunction with detailed examinations of the mechanical properties. The influence of the volume fraction and grain size of TiC nanocrystallites on the coating properties has been examined. The thermal stability of the coatings in terms of critical temperatures, at which the degradation of wear resistance and friction of the coatings starts, are monitored in comparison with the variation of hardness and elastic modulus of the coatings with temperature. In-situ monitoring the thickness of transfer films formed on the counterpart (100Cr6 ball) reveals that the dynamic and super-low friction (µ=0.01-0.05 in air) behavior is directly related to the thickening of transfer films that contributes self-lubrication. The lowest friction and wear rate are obtained when the size of TiC particles become of the same dimension as the separation distance of amorphous hydrocarbon matrix, maximizing also the toughening effects in the composite system. These phenomena have been understood based on a physical model.

Surface Science
Room 202 - Session SS1-TuM
Vibrational Spectroscopy of Surfaces

Moderator: G.P. Williams, Jefferson Labs

8:20am **SS1-TuM1 Direct Observation of Metathesis Reactions on a Carbide Surface: The Surface Chemistry of Multiple Bonds.***, **M. Siaj**, P.H. McBreen,* Université Laval, Canada

Well-defined metal ligand complexes are a feature of organometallic chemistry, and have long served as a guide to understanding chemisorption systems. However, the entire area of metal-ligand multiple bond chemistry appears to have almost no counterpart in surface science. Reports of surface alkylidene species, M=CR1R2 where M is a single metal atom, are extremely rare. Metal-alkylidenes are catalysts for metathesis chemistry, one of the most powerful synthetic methodologies in modern organic, polymer and materials science. Hence, for a variety of applications, it is very important to develop metathesis chemistry on extended surfaces. An extensive set of surface spectroscopy data will be used to show that alkylidene groups can be prepared and isolated on the surface of molybdenum carbide. Futhermore, it will be shown that vibrational spectroscopy may be used to perform in-situ monitoring of cross-metathesis and ring opening polymerization reactions, isolating both initiator and propagator species. These results illuminate both the reaction mechanism for heterogeneous metathesis and the unique ability of the metal carbide surface to promote highly selective catalysis.

8:40am **SS1-TuM2 Strategies for DFT Modeling of Experimental Surface Vibrational Modes***, **P. Uvdal**,* Lund University, Sweden*; M.P. Andersson,* Technical University of Denmark

We have explored and developed electronic structure calculations as a tool for the interpretation of experimental vibrational spectra of surface adsorbates. By combining high sensitive surface infrared spectroscopy and density functional calculations details in the spectra, beyond the harmonic level, can be analyzed. These details allow us to extract new information about the physical properties of adsorbed molecules, information not available using the harmonic or normal mode approximation. For instance the C-H stretch region of organic adsorbates contains often more than 50% of the informational content of the vibrational spectrum. Any proper assignment of this region can, however, not be done at the normal mode level. It requires a treatment, which includes anharmonic coupling between fundamental C-H stretch modes and binary/overtone modes of CH3 and CH2 bending modes. This complicates the comparison between calculations and experiments. Base on the concept of spectral moment or intensity weight average one can however obtain the unperturbed frequency of a vibrational mode, e.g. the C-H stretch mode in methoxy. This frequency can then directly be compared to the frequency determined by calculations in the absence of anharmonic coupling between fundamental and binary/overtone modes. This new concept is discussed and related to our recently determined new scaling factor for harmonic vibrational frequencies using the B3LYP density functional method with the triplezeta basis set 6-311+G(d,p)@footnote 1@. @FootnoteText@ @footnote 1@M. P. Andersson and P. Uvdal, J. Phys. Chem. A 109, 2937 (2005).

9:00am **SS1-TuM3 Freidel Oscillations: S and CO Metal Mediated Interactions***, X.F. Hu, **C.J. Hirschmugl**,* University of Wisconsin-Milwaukee

The coadsorption of CO and S on Cu(100) is examined to gain a deeper understanding of metal-mediated interactions between co-adsorbates. Using a combination of IRAS, Auger Electron Spectroscopy (AES) and TDMS, we find that CO adsorbates do not occupy the first and second nearest-neighbor adsorption sites of S adatoms, but are strongly bound to third-nearest neighbor sites. Simple site-blocking can explain the absence of CO adsorption at first-nearest neighbor sites. However, we attribute the second- and third-nearest neighbor results to S-induced changes in the LDOS. A local minimum is induced at second-nearest sites, suppressing CO adsorption, but a local maximum at third-nearest sites enhances the C-metal bonding strength. Bonding to these sites is stronger than even on the clean Cu(100) surface. Furthermore, the C-O stretch frequency and the dipole-dipole coupling are affected by the S coverage. For a low S coverage, where dipole-dipole coupling is still dominant, a Coherent Potential Approximation (CPA) treatment of dipole-dipole coupling is used to estimate the spatial extent reffective of S and CO substrate-mediated interactions. reffective is found to be between 6 ~ 7 Å. This work shows that S affects the CO adsorption in three ways: making adsorption sites electronically unfavorable, affecting the interface bonding between CO and Cu, and reducing the CO intermolecular interaction.

9:20am **SS1-TuM4 Attenuated Total Reflection Infrared Spectroscopy and Nanoparticles: A New Tool for Probing Adsorption (CO, NH@sub 3@) on Planar Model Catalysts (Rh)***, **C.M. Leewis**, M.C.M. Van De Sanden,* Eindhoven University of Technology, The Netherlands*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands*; J.W. Niemantsverdriet,* Eindhoven University of Technology, The Netherlands

Attenuated total internal reflection Fourier transform infrared spectroscopy (ATR-FTIR) is used to study adsorption and/or decomposition of CO and NH@sub 3@ on Rh nanoparticles. The silicon ATR crystal (25 reflections, 45°) with a 50 nm thick hydroxylated thermal SiO@sub 2@ layer acts as the support for the nanoparticles. These are spincoated from a RhCl@sub 3@ solution in water followed by reduction in H@sub 2@ at 200°C. X-ray Photoelectron Spectroscopy (XPS) shows the reduction to Rh@super 0@ and the removal of Cl. Atomic Force Microscopy (AFM) shows a distribution of 200 particles per µm@super 2@, which are ~3 nm in height. The ATR-FTIR experiments are performed in UHV without exposing the crystal bevels and backside (both without oxide and Rh) to the gases. For a 4 cm@super -1@ resolution, a sensitivity of reflectance as low as 5x10@super -5@ absorbance units in the region 2000-3500 cm@super -1@ can be reached. CO exposure validates the detection of species on the nanoparticles, since CO does not interact with the support. Linearly adsorbed CO on Rh is observed at 2023 cm@super -1@. No bridged CO or geminal dicarbonyls are observed. For ammonia, interaction with the silica OH groups is observed around 2900 cm@super -1@ in combination with negative unperturbed OH peaks between 3500 and 3700 cm@super -1@. In addition, N-H bend (1634 cm@super -1@) and stretch (3065, 3197 cm@super -1@) vibrations are observed for substrate temperatures between 20°C and 150°C. The latter correspond to N-H on Rh, as verified with a sample without Rh, and remained after evacuation, suggesting strongly bound species. For 75°C and 100°C, additional peaks at 3354 and 3283 cm@super -1@ are observed, possibly due to NH@sub 2@ intermediates. ATR-FTIR is therefore a powerful technique for probing adsorbates on supported nanoparticles.

9:40am **SS1-TuM5 Formation of C-H and N-H bonds on the Pt(111) Surface as Studied with Reflection Absorption Infrared Spectroscopy**, *R. Deng, E. Herceg, K. Mudiyanselage, J. Jones,* ***M. Trenary,*** University of Illinois at Chicago **INVITED**

The reaction of hydrogen with atomic species adsorbed on transition metal surfaces is a key step in many important catalytic processes. However, many surface probes are not sensitive to hydrogen so the detection and characterization of processes in which hydrogen forms bonds to other elements on surfaces has been difficult. Recent advances in the sensitivity of surface infrared spectroscopy allows surface intermediates with very weak IR absorption bands to be unambiguously detected. It is well known that the complete dehydrogenation of various hydrocarbons eventually leads to graphitic monolayers on platinum surfaces, although the exact forms of the surface carbon prior to graphite formation are still undetermined. Surface carbon has been prepared by the dehydrogenation of ethylene and acetylene on Pt(111) through exposure at 750 K. Subsequent hydrogen exposure leads to clear infrared features due to methylidyne (CH), ethylidyne (CCH@sub 3@), and ethynyl (CCH). These results demonstrate that C atoms and C@sub 2@ molecules exist as stable species on the surface. An ordered (2x2) layer of N atoms can be prepared on Pt(111) through the oxidation of ammonia in which all of the hydrogen and oxygen are removed through the desorption of water. Subsequent hydrogen exposure leads to a sharp and intense infrared band at 3320 cm@sup -1@ due to the NH species. Quantitative determinations of the NH and N coverages through temperature programmed desorption measurements indicate that only a small fraction of the surface N atoms are reactive towards hydrogen. The NH species can not be further hydrogenated to NH@sub 2@ or NH@sub 3@ under the conditions used in these experiments.

10:20am **SS1-TuM7 RAIRS Signature of the Ordered Methyl Bromide Monolayer on Pt(111)**, ***I. Samanta,*** *T. Schwendemann,* University of Virginia; *T. Kunstman,* University of Essen, Germany; *I. Harrison,* University of Virginia

Scanning tunneling microscopy (STM) reveals that methyl bromide (CH@sub 3@Br) adsorbed on a Pt(111) surface can order into a relatively close packed monolayer of upright molecules even though the dipole moment of these rod-like molecules is substantial (1.8 Debye in the gas phase). The formation kinetics of the ordered (3 x 5) structure can be slow at temperatures less than 100 K. The unit cell contains four CH@sub 3@Br molecules of two kinds oriented with C-Br axis along the surface normal. The CH@sub 3@Br saturation coverage is estimated to be 0.27 ML by STM. Other ordered structures are observed at lower coverages. The evolution of ensemble-averaged reflection absorption infrared spectroscopy (RAIRS), thermal programmed desorption (TPD) spectroscopy, and photochemical dynamics experiments on CH@sub 3@Br/Pt(111) as a function of coverage will be discussed in light of the microscopic structures observed by STM. The RAIRS signature of the ordered CH@sub 3@Br monolayer is the disappearance of the @nu@@sub 5@ asymmetric CH@sub 3@ deformational mode near 1411 cm@super -1@ and the adsorption-site induced splitting of the @nu@@sub 2@ symmetric CH@sub 3@ deformational mode into a doublet at 1271 cm@super -1@ and 1277 cm@super -1@ with fwhms of just 3 cm@super -1@.

10:40am **SS1-TuM8 Adsorption on Carbon Nanotubes Studied Using Polarization-Modulated Infrared Reflection-Absorption Spectroscopy**, ***V.M. Bermudez,*** Naval Research Laboratory

Single-wall carbon nanotubes (SWNT's), deposited onto an Al substrate from a liquid suspension, have been cleaned by annealing in UHV. The effects of exposing the sample in situ to atomic H (or D) and/or to DMMP [dimethyl methylphosphonate, (CH@sub 3@O)@sub 2@(CH@sub 3@)P=O] were then studied using polarization-modulated infrared reflection-absorption spectroscopy. Atomic H reacts preferentially near strained or defective regions in the nanotube wall to produce a spectrum consistent with alkane-like species (>CH@sub 2@ and CH@sub 3@). Only a small fraction of the >C=C< sites in the nanotube wall react with H, and there is no clear evidence for monohydride (>C(H) C(H)<) species. For DMMP, data were obtained under steady-state conditions in reagent pressures in excess of half the room-temperature vapor pressure. Adsorption occurs via the P=O group with a coverage that depends on the ambient pressure. Varying the DMMP coverage by changing the pressure causes changes in the spectrum that can be related to the strength of the DMMP/SWNT interaction. Pre-adsorbed H is seen to have little or no effect on the subsequent adsorption of DMMP. For DMMP, the molecular features are superimposed on a broad, smoothly-varying background that can be related to adsorption-induced changes in the Drude parameters characterizing the SWNT free-carrier density and scattering lifetime. Data were also obtained during exposure to @super 16@O@sub 2@ or @super 18@O@sub 2@. As in the case of atomic H, evidence is seen for preferential reaction near strained or defective regions, but no vibrational modes of adsorbed O or O@sub 2@ are detected.

11:00am **SS1-TuM9 Nanoporous Gold As a Novel Highly Active Substrate for Surface-Enhanced Raman Spectroscopy**, *J. Biener, J.R. Hayes, S.O. Kucheyev, T. Huser, C.E. Talley, A.M. Hodge,* ***A.V. Hamza,*** Lawrence Livermore National Laboratory

Surface-enhanced Raman-scattering (SERS) spectroscopy has attracted considerable interest in recent years due to the possibility to reach the single molecule detection limit. Colloidal solutions of gold or silver with particle sizes in the submicron range are most commonly used as SERS active substrates. However, the limited stability and reproducibility of metal colloids currently hampers their use as SERS substrates. Here, we report on the development of nanoporous gold (np-Au) as a novel, highly active SERS substrate. The SERS activity was probed using crystal violet as a test molecule. The significant Raman enhancement observed seems to be a consequence of the nanoscale surface roughness and curvature of np-Au. The material is prepared by dealloying Ag-Au alloys, and exhibits an open sponge-like morphology of interconnecting Au ligaments with a typical pore size distribution on the nanometer length scale. The dimensions of both pores and ligaments can be further fine-tuned by chemical and/or thermal treatments. Our ultimate goal is the development of an affordable, stable, reproducible, and highly active substrate for SERS-based chemical sensors. 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.

11:20am **SS1-TuM10 Vibrational and Photoelectron Spectroscopy of Formic Acid and Water Coadsorbed on Au(111) Surfaces: Chemical Interaction and Compound Formation**, ***G. Pirug,*** *M. Kazempoor,* Forschungszentrum Jülich GmbH, Germany

The coadsorption of formic acid (HCOOH) and water (H@sub 2@O) has been studied on Au(111) single crystal surfaces by means of vibrational spectroscopy (HREELS) and photoelectron spectroscopy (XPS) in the temperature range between 90 K and 200 K. Formic acid adsorbs at 90 K molecularly with vibrational modes characteristic for solid formic acid. Annealing results in a complete desorption at 190 K. Upon sequential adsorption of formic acid and water at 90 K no significant chemical interaction can be deduced from the vibrational signatures and the core level photoelectron binding energies. Independent of the sequence of exposure coadsorption or layered growth without intermixing is observed in the monolayer and the multilayer regime, respectively. Heating of the coadsorbed layer to about 140 K results in the formation of a new surface complex with characteristic vibrational losses at 190, 590 and 1000 cm @super -1@. Based on these frequencies and supported by the corresponding stoichiometries as deduced from XPS possible compounds will be discussed. Upon further annealing this complex decomposes leaving only molecularly adsorbed formic acid on the surface at 160 K. These results will be discussed in the light of recent findings for the electrochemical oxidation of formic acid on Au surfaces.

11:40am **SS1-TuM11 STS Vibrational Study of 1,3-cyclohexadiene on Si(100) Surface**, ***B. Naydenov,*** *J.J. Boland,* Trinity College Dublin, Ireland

Scanning tunnelling spectroscopy was performed on 1,3-cyclohexadiene modified Si(100) surface at 5K. Degenerated N-type semiconductor and platinum covered tungsten tips were used. For the first time a vibrational spectrum of chemisorbed molecule on semiconductor surface was obtained. The spectroscopic conditions involved small tip-sample separations, far from the normal imaging conditions, and for wish the simple tunnelling picture involving overlapping wave function tails is no longer valid. Under such conditions significant forces and weak chemical bond occurs between the tip and the surface. The vibrational features and the tunnelling barrier height variations with the tip-sample distance will be discussed.

Surface Science
Room 203 - Session SS2-TuM

Defects on Oxide Surfaces

Moderator: D. Bonnell, University of Pennsylvania

8:20am **SS2-TuM1 Structure and Properties of SrTiO@sub 3@ (100) Surface***, R. Shao,* ***M. Nikiforov****, D. Bonnell,* University of Pennsylvania

The surfaces of Strontium Titanate, one of the simplest perovskites, have been intensively studied because of its relevance to catalysis, environmental interactions and electronic devices. The (100) surface can terminate in either Sr-O or Ti-O planes. A number of reconstructions have been found on this surface depending on processing conditions. We have been able to stabilize atomically smooth (100) surfaces with unit cell (0.4 nm) and half unit cell (0.2 nm) steps assuring the presence of both types of terminations. Scanning tunneling spectroscopy of the two termination planes exhibits differences in electronic structure that are related to the proximity of Ti d orbitals near the surface. An orientational relationship between reconstructions and step edge direction is quantitatively related to strain from a systematic series of surfaces with different miscut angles. Finally the surface relaxation and electronic structure at low temperatures will be presented.

8:40am **SS2-TuM2 Oxygen Adsorption, Diffusion, and Reaction on a Reduced TiO@sub 2@(110) Surface***,* ***D. Pillay****, G. Hwang,* The University of Texas at Austin

The rutile TiO@sub 2@(110) surface has been widely used as a catalyst for photochemical reactions and a support for transition metal catalysts. Molecular oxygen adsorption plays an important role in determining the activity of TiO@sub 2@ and supported metal catalysts. Surface bound oxygen species may directly influence chemical and photochemical processes occurring on TiO@sub 2@. In addition, O@sub 2@ exposure leads to significant structural changes of supported metal particles, which may in turn affect their catalytic activity. It has been found that O@sub 2@ adsorbs on TiO@sub 2@(110) only when O-vacancies are present. Despite its importance, however the chemistry and dynamics of adsorbed oxygen species on a Au-covered reduced TiO@sub 2@(110) surface are still unclear. Using density functional theory calculations, we have investigated the adsorption and diffusion of oxygen species on the reduced TiO@sub 2@(110) surface. We have found that O@sub 2@ strongly binds not only to O-vacancies, but also to Ti(5c) neighbors, due to delocalization of unpaired electrons arising from the removal of neutral bridging oxygen atoms. Our results show that O@sub 2@ can jump across an oxygen vacancy and diffuse along a Ti(5c) row, with a moderate barrier that is significantly altered by the density of O vacancies. Based on our calculation results, we will discuss the diffusion and healing of O vacancies associated with O@sub 2@ adsorption, as a function of the vacancy density. We will also present the structure and energetics of higher coverage O@sub 2@ adsorption, as well as CO oxidation mechanisms on the reduced TiO@sub 2@(110) surface.

9:00am **SS2-TuM3 High-Resolution Scanning Tunneling Microscopy Studies of Surface Reactions on Rutile TiO2(110)***,* ***F. Besenbacher,*** University of Aarhus, Denmark **INVITED**

Transition-metal oxide surfaces play an important role in a wide range of applications, e.g. heterogeneous catalysis, photoelectrolysis, biocompatibility and sanitary disinfection. Defects like oxygen vacancies often dominate electronic and chemical properties of transition-metal oxide surfaces. In recent studies on a prototypical model oxide system (rutile TiO2(110) surface) we exploited our high-resolution, variable-temperature and fast-scanning Aarhus STM to study how oxygen vacancies influence surface and interface reactions. Water dissociation on TiO2 is of fundamental interest as an example of a simple surface chemical process with important applications. In high-resolution STM experiments, we unambiguously identify surface oxygen vacancies and hydroxyl groups. Controlled voltage STM pulses allow us to desorb OH groups only; O vacancies remain unaffected. Through STM images and time-resolved movies, we determine the active site responsible for the water molecule dissociation on TiO2(110). At low H2O exposures, O vacancies dissociate water molecules by transferring one proton to a nearby oxygen atom, forming two hydroxyl groups for every vacancy. At elevated exposures, a novel water dissociation channel is seen and will be described in detail. The amount of water dissociation is not limited by the density of oxygen vacancies on the clean surface as proposed earlier in literature. Extended oxygen exposure on TiO2(110) will lead to restoichiometrization of the support, thus markedly reducing its reactivity. An atomic-scale understanding of the healing process is still lacking, but it is thought to be a simple mechanism where a single O2 molecule heals two vacancies subsequent to a dissociative process. Using high-resolution STM and TPD measurements, we investigate the interaction of O2 from the gas phase with different surface defects (O vacancies, OH groups) on TiO2(110).

9:40am **SS2-TuM5 Surface Reconstruction Variations on Barium Titanate (100)***,* ***R. Shao****, D. Bonnell,* University of Pennsylvania

BaTiO@sub 3@, is a prototype ferroelectric compound and a simple model for interactions in complex oxides. Recently the effect of ferroelectric dipoles on interactions of surfaces has been examined as it relates to domain specific chemical reactivity. Scanning probe microscopy is the obvious probe of local surface reactions; however, it has proven difficult to obtain reproducible atomically smooth surfaces because of its tendency toward non stoichiometry and carbonate formation. In this work, we have determined the sequence of high temperature annealing in oxidizing and reducing atmospheres with which BaTiO@sub 3@ (100) surfaces can be produced with unit cell (0.4 nm) and half unit cell (0.2) step heights. These steps correspond to different lattice plane terminations. Atomic resolution STM is used in conjunction with LEED/AES and Scanning Surface Potentiometry (Kelvin Probe Microscopy) to compare the geometric and electronic structures that occur on these surfaces as a function of thermal history. Differences in electronic structure determined from tunneling spectroscopy are compared to theoretical predictions.

10:00am **SS2-TuM6 Defects Modeled with Vicinally-Stepped Oxide Surfaces: the Adsorption of Bromobenzene on NiO(100)***, E.M. Marsh, S.C. Petitto,* ***M.A. Langell,*** University of Nebraska-Lincoln

The chemical reactivity of a metal oxide surface is often dominated by its defect properties. However, at naturally-occurring levels these defects are often present in low concentrations and as only one of a range of defect types making their effect on surface reactivity difficult to isolate. We have modeled oxide step defects with periodically-stepped NiO(100) substrates, where the predominant defect type and concentration can be readily controlled, and have investigated the ability of the stepped substrates to adsorb and dissociate bromobenzene (C@sub 6@H@sub 5@Br). The surfaces were characterized using Auger electron (AES) and x-ray photoelectron (XPS) spectroscopies, low energy electron diffraction (LEED), high resolution electron energy loss spectroscopy (HREELS) and thermal desorption mass spectrometry (TDS). In particular, the geometry of the adsorbate is correlated with short terrace widths and this in turn affects the dissociative nature of the adsorbate interaction.

10:20am **SS2-TuM7 Structure, Defects, and Adsorption on Metal Oxide Surfaces***,* ***U. Diebold,*** Tulane University **INVITED**

In recent years, the surface science of metal oxides has experienced a remarkable increase in terms of research papers published, systems studied, and level of detail of the obtained information. A long-standing paradigm -- that surface defects on oxides are dominant reactivity centers -- is now scrutinized with scanning probe techniques. In this talk, I will give a representative overview of surface structural and adsorption studies on various surface orientations of TiO@sub 2@, ZnO, and SnO@sub 2@. Our experimental investigations are significantly enhanced through collaborations with theoretical groups.

11:00am **SS2-TuM9 Controlling Surface Reactivity of SnO@sub 2@(101): Dissociative and Molecular Water Adsorption***,* ***M. Batzill,*** *U. Diebold,* Tulane University

Water adsorbs dissociatively on many oxide surfaces. In such cases undercoordinated surface oxygen atoms accept a proton and the remaining water-OH- adsorbs on surface cation sites. Thus the surface reactivity towards water dissociation may be tuned by controlling the number of undercoordinated surface oxygen atoms (Broensted base sites). On SnO@sub 2@(101) such a control over the surface composition can be exerted and the surface can be prepared with and without terminating oxygen atoms.@footnote 1@ Here we show by valence band photoemission that these two surfaces show different activity towards water adsorption. Surfaces without bridging oxygen adsorb water weakly while dissociation is observed on surfaces exhibiting terminating oxygen. The different activity of the surfaces is also apparent from water induced band bending. Dissociative adsorption causes downward band bending of ~0.35 eV which consequently causes a large increase in the surface conductivity of the SnO@sub 2@ sample. The latter is measured using a novel approach utilizing surface charging as a conductivity probe. @FootnoteText@ @footnote 1@ M. Batzill, A.M. Chaka, U. Diebold, Europhys. Lett. 65, 61 (2004).

11:40am **SS2-TuM11 The Reaction of Water over the Stoichiometric and Defected Surfaces of Uranium Dioxide: a High Resolution XPS Study***, S.D. Senanayake, G.I.N. Waterhouse,* The Univ. of Auckland, New Zealand*; A.S.Y. Chan,* Rutgers, The State Univ. of New Jersey*; D.R. Mullins,* Oak Ridge National Lab.*; T.E. Madey,* Rutgers, The State Univ. of New Jersey*; **H. Idriss**,* The Univ. of Auckland, New Zealand

The chemistry of the uranium oxides is complex and historically been important to many aspects of nuclear technology. A recent study has shown using XPS that argon ion sputtering of the UO@sub 2@ surface can form a stable reduced oxide surface (UO@sub 2-x@) due to creation of oxygen defects.@footnote 1@ This work uses high resolution photoelectron spectroscopy (HRXPS) performed at the beam line U12a at the National Synchrotron Light Source/BNL to investigate the effect of this defect formation process. Sputtering at 300 and 95K gave different defect distributions. The reduced surface has a complex set of oxidation states lower than that of U@super +4@ including U metal (U@super 0@). Previous investigations made on the reactivity of water vapor on polycrystalline UO@sub 2@@footnote 2@ and defected single crystal UO@sub 2-x@ surface have revealed complex reaction pathways to the production of H@sub 2@ and XPS has further confirmed adsorbate induced oxidation of the surface.@footnote 1@ This work aims to further examine the effect of D@sub 2@O adsorption on the stoichiometric and sputter reduced surfaces of UO@sub 2@ at 300 and 95K. The effects of the thermal chemistry and oxidation of the surface is studied using temperature programmed XPS (TPXPS). In particular, the formation of D@sub 2@O ice at low temperature and dissociated OD species versus the role of defects in this heterogeneous interplay is examined. @FootnoteText@ @footnote 1@ Senanayake S.D., Idriss H., Surf. Sci. 563 (2004) 135.@footnote 2@ Senanayake S.D., Rousseau R., Colegrave D., Idriss H, J. Nucl. Mater. In press.

Thin Films
Room 306 - Session TF-TuM
Atomic Layer Deposition - Oxides

Moderator: H. Kim, Pohang University of Science and Technology, Korea

8:20am **TF-TuM1 Atomic Layer Deposition of Titanium Oxide Thin Films using O@sub 3@ for MIM Capacitor of Next Generation Memory Devices***, **S.K. Kim**, K.M. Kim, C.S. Hwang,* Seoul National University, Korea

TiO@sub 2@ films were deposited using a travelling-wave type ALD reactor on a bare-Si (100) wafer, sputtered and ALD Ru, and sputtered Pt electrodes at a wafer temperature of 250°C. TiO@sub 2@ thin films was grown using Ti(OC@sub 3@H@sub 7@)@sub 4@ and O@sub 3@ as the precursor and oxidant, respectively. The dielectric constants of these TiO@sub 2@ films are 83 between 100 for the films on Ru electrodes. Crystalline structure of TiO@sub 2@ films on various substrates was investigated to understand the origin of higher k values of TiO@sub 2@ films on Ru substrates. XRD results of TiO@sub 2@ films on various substrates show that the TiO@sub 2@ films on Si and Pt substrates have anatase structure whereas the films on Ru substrates have rutile phase grains. This means that the growth of rutile TiO@sub 2@ is related to the kind of substrate. The growth of rutile TiO@sub 2@ on Ru substrate is induced by the formation of RuO@sub 2@, which has almost identical ion arrangements in its rutile structure, at the TiO@sub 2@/Ru interface. For the application of the material and ALD process to DRAM devices, TiO@sub 2@ films were grown on contact hole structured Ru electrodes and the dielectric properties of Ru/TiO@sub 2@/Ru 3-D capacitor were investigated. The conformity in film thickness and dielectric properties over the entire structured surface was confirmed by capacitance variation vs. hole surface area experiments. Also, addition of Al as an acceptor in TiO@sub 2@ films was tried to improve the leakage properties of TiO@sub 2@ films due to a rather high leakage current density of TiO@sub 2@ films. Although toxeq. of doped-TiO@sub 2@ films is smaller than that of undoped-TiO@sub 2@ films, leakage current density of doped-TiO@sub 2@ films is much lower than that of undoped-TiO@sub 2@ films.

8:40am **TF-TuM2 Characteristics of Atomic Layer Deposited TiO@sub2@ Films and its Photocatalytic Activity***, **D.H. Kim**, R. Pheamhom,* Chonnam National University, South Korea

Titanium dioxide has many attractive physicochemical properties and thus lends itself to various applications such as optical coatings for anti-reflection, high dielectric layers for electronic devices, biocompatible coatings for biomaterials, and photosensitive layers for photocatalysts and solar cells. In this work, tetrakis(dimethylamido) titanium (TDMAT) has been evaluated as a possible precursor for TiO@sub 2@ ALD using H@sub 2@O@sub 2@ as a counter-reactant. We have explored the effects of deposition temperature, reactants pulse and purging time on the film growth rate to optimize the ALD process for TiO@sub 2@ preparation using TDMAT. Self-limiting reaction was possible, as supported by saturated film growth rate and the linear property of the film growth depending on the number of cycles. Film growth rate, surface morphology, crystallinity, and conformality on the deposition temperature along with the photocatalytic activity of the ALD TiO@sub 2@ in decomposing methylene blue in aqueous solution will be presented.

9:00am **TF-TuM3 Atomic Layer Deposition of SrTiO@sub 3@ Films Having a High Thickness- and Cation-Composition Conformality Over a Severe Contact Hole Structure***, **O.S. Kwon**, S.W. Lee, C.S. Hwang,* Seoul National University, Korea

SrTiO@sub 3@ (STO) thin films were grown on Si wafer and Ru-coated Si wafers, respectively, by an atomic-layer-deposition (ALD) technique using conventional metal organic precursors, Sr(C@sub 11@H@sub 19@O@sub 2@)@sub 2@ (Sr(thd)@sub 2@) and Ti(Oi-C@sub 3@H@sub 7@)@sub 4@ (TTIP) as Sr- and Ti-precursors, respectively, with a remote-plasma activated and thermal H@sub 2@O vapor as oxidant. Although the each precursor exhibited ALD reaction with the remote-plasma activated H@sub 2@O vapor, STO exhibited quite different deposition behavior with the bubbling temperature of Sr(thd) @sub 2@. The cation stoichiometry of STO films was dramatically improved when the bubbling temperature of Sr(thd) @sub 2@ < 200°C (melting temperature of Sr(thd) @sub 2@) irrespective of the type of oxidants. Furthermore, cation composition conformality over the severe contact hole structure (0.13µm opening diameter with an aspect ratio of 8) was highly improved when the Sr(thd)@sub 2@ bubbling temperature was 180°C. The thickness step coverage over the entire contact hole was >95%, and the variation of cation composition was very small (< 3%). The different degree of oligomerization of Sr(thd)@sub 2@ with the bubbling temperature was supposed to be the reason for these phenomena. Electrical properties of STO films grown by ALD were highly dependent on the amount of oxidant. Leakage current density of STO films with lower oxidant supply was too high to measure the dielectric properties. The high leakage property was directly related to the binding energy shift into high binding energy direction of Sr 3d peak position in the XPS analysis. The leakage current density of STO films with sufficient oxidant was reduced and the binding energy shift of Sr 3d peak was reduced. Equivalent oxide thickness < 1nm and leakage current density < 10@super -6@A/cm@super 2@ at 1V were obtained by the optimized two step deposition and post-annealing processes.

9:20am **TF-TuM4 Selective Atomic Layer Deposition (ALD) for Fabrication of Metal and Oxide Nanotubes***, **J.Y. Kim**,* Kookmin University, Korea, Rep. of Korea*; D. Jeong, S. Won, H. Shin, J. Lee,* Kookmin University, Korea

In this study, we have fabricated various metal and oxide nanotubes using selective atomic layer deposition (ALD). We easily control the nanotubes shape and make high aspect ratio nanotubes by selective ALD using SAMs such as OTS(octadesyl-tetrachlorosilane). We avoid unnecessary deposition on top of nanotemplates such as poly-carbonate, which results in stand alone nanotubes without connection. The selective ALD is performed on sacrificial nanotemplates with pore sizes of 30 - 200nm. The template were commercial available polycarbonate (PC) and anodic aluminum oxide (AAO) with various hole sizes and thicknesses. After deposition, template was removed by wet etching. We successfully obtain metal (Cu,Co) and oxide(ZrO2,TiO2) single material nanotubes. In addition, metal/oxide double wall nanotubes are fabricated by sequential ALD process. We make metal oxide nanotubes and measure various properties using high resolution-transmission electron microscope (HR-TEM), field emission-scanning electron microscope (FE-SEM), selective area electron diffraction (SAED) patterns, X-ray diffractionmeter (XRD). We also characterize electrical properties of the nanotubes using conducting-atomic force microscope (AFM). The authors gratefully acknowledge the financial support through center for nanostructured materials technology by Korean ministry of science and technology (03K1501-02410).

9:40am **TF-TuM5 Laterally Graded Films and Multilayers Using Atomic Layer Deposition with a Slit Doser and Substrate Translation***, **F.H. Fabreguette**, S.M. George,* University of Colorado

Laterally graded multilayers have a bilayer spacing that continuously changes versus spatial position. These graded multilayer structures are important for x-ray collimation and x-ray focusing. Recently, optimized W/Al@sub2@O@sub3@ superlattices grown using atomic layer deposition (ALD) displayed an excellent x-ray reflectivity (XRR) of 96% at

@lambda@=1.54 Å. To obtain laterally graded W/Al@sub2@O@sub3@ multilayers, the normal conformality of ALD must be circumvented by preventing ALD on the entire substrate. Laterally graded multilayers can be fabricated using a slit doser to localize reactant delivery in a viscous flow gas stream. The substrate is then translated relative to the slit doser with a magnetic linear translator. Since the viscous flow entrains the reactants and moves them downstream, substrate translation upstream of the slit doser prevents ALD on the entire substrate. A laterally graded Al@sub2@O@sub3@ ALD film was initially demonstrated by translating the substrate relative to the slit doser during Al@sub2@O@sub3@ ALD reaction cycles. Variable angle ellipsometry and XRR quantified a varying Al@sub2@O@sub3@ film thickness grown on a Si(100) wafer with a length of 6 inches. Changes in leakage current density and capacitance confirmed the Al@sub2@O@sub3@ thickness gradient. In addition, a laterally graded ZnO/Al@sub2@O@sub3@ multilayer was grown and characterized using XRR. The angle of the first Bragg peak revealed a bilayer spacing that changed as expected versus spatial position.

10:00am **TF-TuM6 Coating Nanoparticles by Atomic Layer Deposition in a Rotary Fluidized Bed Reactor: Al@sub 2@O@sub 3@ ALD on ZrO@sub 2@**, ***J.A. McCormick***, *A.W. Weimer, S.M. George,* University of Colorado at Boulder

Ultrathin and conformal Al@sub 2@O@sub 3@ films have been grown by atomic layer deposition (ALD) on ZrO@sub 2@ particles with diameters of 60 nm and 400 nm using sequential exposures of trimethylaluminum and H@sub 2@O. This Al@sub 2@O@sub 3@ ALD on gram-scale quantities of high surface area ZrO@sub 2@ nanoparticles was performed in a novel rotary fluidized bed reactor. The rotary fluidized bed reactor consisted of a stainless steel porous metal cylinder that rotated inside a vacuum system. The nanoparticles were contained inside the porous metal cylinder and the gaseous reactants and products could easily diffuse through the porous walls without particle loss. A magnetically coupled rotary motion feedthrough rotated the porous metal cylinder and provided a fluidization-like mixing between the particles and the reactants. The Al@sub 2@O@sub 3@ ALD films were deposited on the ZrO@sub 2@ nanoparticles at 180°C with a growth rate of 1.8 Å/cycle. The composition of the Al@sub 2@O@sub 3@ ALD coating was verified using Auger electron spectroscopy, x-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy. Transmission electron microscopy and BET surface area analysis were utilized to determine the conformality of the Al@sub 2@O@sub 3@ ALD coating and to check for particle coalescence. The Al@sub 2@O@sub 3@ ALD film uniformly coats the primary ZrO@sub 2@ particles and there was no evidence for any particle coalescence.

10:20am **TF-TuM7 The Atomic-Layer-Deposited HfO@sub 2@ Gate Dielectric Films; Chemistry of Interface and Electrical Performances**, *T.J. Park, M.J. Cho, S.H. Hong, M.H. Seo, J.H. Kim, J.H. Park,* ***C.S. Hwang,*** Seoul National University, Korea **INVITED**

HfO@sub 2@ thin films were deposited on HF-dipped Si wafers at temperatures ranging from 250 to 300°C using an atomic-layer-deposition technique with N-containing Hf[N(CH@sub 3@)@sub 2@]@sub 4@, Hf[N(CH@sub 3@)(C@sub 2@H@sub 5@)]@sub 4@ or Hf[N(CH@sub 3@)(@sub 2@H@sub 5@)]@sub 3@[OC(CH@sub 3@)@sub 3@] and H@sub 2@O or O@sub 3@ as the precursor and oxidant, respectively. A thin interfacial SiN@sub x@ layer was spontaneously formed at the HfO@sub 2@/Si interface during film growth. This interfacial SiN@sub x@ layer played a critical role in improving the thermal stability and interfacial trap (D@sub it@) property. D@sub it@ of < 5 x 10@super 10@ cm@super -2@eV@super -1@ near the mid-gap energy states was obtained from most of the process conditions but it usually suffer from the degradation by high temperature post-deposition annealing (PDA) at temperatures > 800°C. The adoption of O@sub 3@ oxidant reduced carbon impurity concentration and made the film more amorphous compared to the films grown using H@sub 2@O as oxidant. Although ozone was effective in reducing the impurity concentration, the higher concentration slightly deteriorated the dielectric performance. Investigation of the interface states using X-ray photoelectron spectroscopy revealed that the excessive oxygen incorporated during the film growth made the interfacial sub-oxide species (SiO, Si@sub 2@O@sub 3@ and silicate) and SiO@sub 2@ coordinate more with oxygen. This was further confirmed by the MOSFET performance comparison fabricated with HfO@sub 2@ gate dielectrics using different O@sub 3@ concentration. An electron effective mobility of ~ 65% of the MOSFET with SiO@sub 2@ as gate dielectric was obtained from the stoichiometric HfO@sub 2@ gate dielectric film. The effective mobility from the MOSFET with the oxygen excess HfO@sub 2@ film was only ~ 45 %.

11:00am **TF-TuM9 Atomic Layer Deposition for the Modification and Stabilization of Localized Surface Plasmon Resonance Nanosensors**, ***J.W. Elam,*** *M.J. Pellin,* Argonne National Laboratory*; A.V. Whitney, R.P. Van Duyne, P.C. Stair, G.C. Schatz, S. Zou,* Northwestern University

Noble metal nanoparticles serve as optical biosensors and chemosensors because of the localized surface plasmon resonance (LSPR) effect. The optical properties of LSPR sensors are strongly influenced by the size, shape and dielectric environment of the nanoparticles. Atomic layer deposition (ALD) can deposit dielectric films with atomic layer precision onto a variety of substrates including noble metals. Consequently, the optical properties of LSPR sensors can be tailored using ALD coatings. In this study, ordered arrays of Ag nanoparticles were coated with ALD Al@sub2@O@sub3@ and the resulting changes in the physical properties of the nanoparticles were explored. Initial experiments examined the nucleation and growth of ALD Al@sub2@O@sub3@ on flat Ag surfaces using quartz crystal microbalance and ellipsometry measurements. Surprisingly, these measurements demonstrated that the Al@sub2@O@sub3@ ALD proceeds on Ag without any nucleation delay. Next, ordered arrays of Ag nanotriangles fabricated using nanosphere lithography were coated using ALD Al@sub2@O@sub3@ at 50 °C. Optical absorption measurements revealed a 6 nm red shift in the LSPR peak for an Al@sub2@O@sub3@ thickness of only 1.6 Å. The LSPR peak continues to red shift with increasing Al@sub2@O@sub3@ thickness up to ~600 Å. These changes are explained well by theoretical analysis using finite element electrodynamics. The Ag nanotriangles were also examined using atomic force microscopy and scanning electron microscopy and these measurements demonstrated that the ALD Al@sub2@O@sub3@ conformally coats the nanotriangles while preserving their initial shape. Preliminary experiments reveal that thin ALD Al@sub2@O@sub3@ layers significantly improve the thermal stability of Ag nanoparticles while retaining strong Raman enhancement, suggesting that ALD coatings will broaden the range of applications for LSPR nanosensors.

11:20am **TF-TuM10 Atomic Layer Deposition (ALD) of Nickel Films Using Amidinate Precursors**, ***V.R. Pallem,*** *K. Kim, J.S. Park, R.G. Gordon,* Harvard University

Atomic layer deposition (ALD) of nickel thin films was demonstrated by using new nickel-amidinate precursors. Here we present a dozen nickel N,N'-Dialkyl-2-alkyl/aryl-amidinate derivatives as potential precursors for ALD. Their physical properties (volatility, thermal stability and chemical reactivity) were tuned by altering the alkyl groups. Nickel-bis(N,N'-di-tert-butylacetamidinate) showed the best overall properties as an ALD precursor. With NH@sub 3@ as a reducing agent at 270°C, self-limiting growth was achieved at a rate of 0.4 Å/cycle. Analyses of the deposited films showed only nickel. Nickel films grown on silicon nitride substrate had resistivity of 81 µ@ohm@-cm. Post-deposition annealing of nickel films on HF-last silicon showed the formation of nickel silicide.

Technology for Sustainability
Room 313 - Session TS-TuM

Fuel Cells, Hydrogen Economy, Sustainable Manufacturing

Moderator: P.J. Maroulis, Air Products and Chemicals, Inc.

9:20am **TS-TuM4 Direct Oxidation of Hydrocarbon Fuels in a Solid Oxide Fuel Cell: Studies of Carbon Formation**, *V.K. Medvedev, L.M. Roen,* ***E.M. Stuve,*** University of Washington

Solid oxide fuel cells (SOFC) provide an opportunity for fuel-flexible fuel cells that operate at higher efficiencies than other types of fuel cells. These advantages arise from the high temperature of SOFC operation, 800-1000 °C, which facilitates direct oxidation and reforming of hydrocarbon fuels and a source of high quality waste heat. This work examines direct oxidation of hydrocarbon fuels on a SOFC installed in a vacuum system with facilities for accurate measurement of fuel and oxygen partial pressures and measurement of reaction products by a calibrated mass spectrometer. The measurements highlight the interplay of fuel oxidation kinetics, carbon deposition on the anode, and transport of oxide ions through the electrolyte. The SOFC consisted of a Gd-doped ceria electrolyte (Gd@sub 0.1@Ce@sub 0.9@O@sub 2@) with platinum anode and cathode. Fuels of study included methanol, ethanol, methane, ethylene, carbon monoxide, and hydrogen. The reactions were studied over the temperature range of 800-1000 °C with fuel and oxygen partial pressures of 0-10 Torr and 0-70

Torr, respectively. Hydrogen, CO, methanol, and ethanol showed similar reaction characteristics, with high open circuit voltages of 0.6 V and above and maximum current densities of approximately 2 mA/cm@super 2@. By contrast, ethylene and methane showed much slower reaction rates, with open circuit voltages of approximately 0.1 V and maximum current densities of approximately 0.01 mA/cm@super 2@. Post-reaction titration of the anode surface with oxygen showed evidence of extensive carbon formation under the low reaction conditions. The dynamic response of the system under changing fuel and oxygen partial pressures provided further evidence of carbon formation. These experiments help establish the mechanism of direct fuel oxidation in solid oxide fuel cells and the conditions for avoiding carbon deposition on the anodes. This work was supported by the Office of Naval Research.

9:40am **TS-TuM5 Hydrogen as an Energy Carrier: Its' Promises and Challenges*, G.R. Keenan,*** Air Products and Chemicals, Inc. **INVITED**

No Abstract Text Submitted

10:20am **TS-TuM7 Development of Sustainable Technology and Practices in the Semiconductor Industry*, W. Worth,*** SEMATECH **INVITED**

The semiconductor industry has for years been held up as an example of a "clean", progressive, and environmentally friendly industry. To maintain this image and to ensure the long-term sustainability of the industry, SEMATECH, the R&D consortium of the major chip manufacturers, has diligently worked for many years on resource conservation including energy, water and chemical reduction. This paper will discuss the ideas that the industry has successfully implemented or is studying in each of these areas. Energy reductions have been achieved through HEPA velocity and tool exhaust reduction, and optimization of onsite nitrogen generation and use. The current focus is on improving tool heat dissipation and tool idle energy use. Similarly, recognizing that the industry uses significant amounts of water for wafer etching, rinsing and chemical mechanical planarization (CMP), SEMATECH has focused on ultra pure water (UPW) recycle, optimization of wafer rinse processes and non-process water use in CMP. More recent efforts have centered on improved CMP slurry utilization and reduction of consumables such as pads and post-CMP clean brushes. In the chemicals arena, the industry is working closely with regulatory agencies globally to reduce emissions of undesirable chemicals such as perfluorocompounds (PFCs) and perfluorooctane sulfonates (PFOS). In addition, SEMATECH and the World Semiconductor Council (WSC) have emphasized the need for more comprehensive and timely access to environment, safety and health (ESH) data for the many new chemicals being introduced into manufacturing to meet the performance needs of the advanced semiconductor products. By providing more data to the technologists as they design the new processes and tools it is hoped the industry can avoid the use of materials that may be unacceptable from a long-term industry sustainability perspective.

Vacuum Technology
Room 200 - Session VT-TuM
Total and Partial Pressure Gauging

Moderator: T. Gessert, National Renewable Energy Laboratory

8:40am **VT-TuM2 New Ignition Devices for Cold-Cathode Gauges*, B.R.F. Kendall,*** Elvac Laboratories*; E. Drubetsky,* Televac Division of The Fredericks Company

The discharge in a cold-cathode gauge does not start immediately when power is applied. In the absence of special starting devices the delay may be quite long, with large variations between successive starts. Average values typically range from seconds at 10@super -6@ Torr to hours or even days at 10@super -11@ Torr. For this reason, gauges which require frequent starting at very low pressures have sometimes been fitted with either radioactive or thermionic emitters to ensure relatively quick and predictable starting. Although effective, these solutions can cause other problems. Many laboratories are now reluctant to handle even weak radioactive sources, while the disturbance to the background pressure caused by some thermionic emitters can be significant. In an attempt to resolve these difficulties, we have tested diamond-like film emitters and electron generator arrays, both of which offer suitable fluxes of cold electrons for gauge starting. We have also made a detailed study of the physical processes occurring during gauge starting with thermionic electron sources. This has led to a very compact low-power emitter which greatly reduces thermal desorption during the starting process. The test gauges were double inverted magnetrons operating at pressures down to the 10@super -11@ Torr range.

9:00am **VT-TuM3 Selecting Vacuum Instrumentation for Your Applications*, C.R. Tilford,*** Independent Consultant **INVITED**

Vacuum users today are offered a wide variety of commercially-available vacuum instrumentation. But selecting adequate or best instruments for a particular application can sometimes be a daunting task since the only well defined parameter may be the cost. This talk will provide information to help users select instruments that will best meet their needs. This will include a brief description of thermal conductivity gauges, capacitance diaphragm gauges, micromachined electromechanical pressure gauges, ionization gauges and residual gas analyzers, and a discussion of the relative advantages and disadvantages of each type. Beyond this, experimental procedures will be described that can be carried out in the user's laboratory to determine important characteristics of specific instruments and, in some cases, make adjustments to optimize performance.

9:40am **VT-TuM5 Results of Performance Dependencies of Bayard-Alpert type Hot Cathode Ionization Gauges Upon Operational Parameters of Their Controllers*, P.C. Arnold,*** Helix Technology Corporation

An evaluation has been performed of the precision required to provide indicated pressure repeatability time-to-time and reproducibility controller-to-controller, with respect to the operational parameters of ionization gauge controllers. Gauge sensitivity of Bayard-Alpert type hot cathode ionization gauges has been studied and the dependence upon parameters of operation has been measured and will be displayed graphically. These measurements will allow a user to compare the precision of the userâ?Ts gauge controller to the needs of accurate pressure indication. The independent parameters varied were anode potential and cathode potential, with either cathode end at the cathode bias potential and with the cathode heating voltage applied at either cathode end, while the other variables of operation were held fixed. The fixed parameters were various electron emission currents, various nitrogen pressures, and several gauges. Another issue in ionization gauge operation is measurement of the base pressure of a vacuum chamber by a gauge attached to that chamber which is a continual problem in practical applications. Test data will be shown demonstrating that the magnitude of electron emission can significantly affect the indicated pumpdown rate observed for the chamber, or can significantly affect the steady state value of the indicated base pressure for a practical chamber in the UHV range.

10:20am **VT-TuM7 Residual Gas Analyzers as Total Pressure Gauges*, M. Maskell,*** Old Dominion University*; P. Adderley,* Jefferson Lab*; G.A. Brucker,* Stanford Research Systems*; C. Day,* Forschungszentrum, Karlsruhe*; G.R. Myneni,* Jefferson Lab

Residual Gas Analyzers (RGAs) provide many benefits over other types of gauges that measure total pressure only. RGAs give information about the specific composition of the residual gas in a vacuum system, and can be used for leak detection and diagnosis of other problems in a vacuum system. When the partial pressure capabilities of an RGA are needed, it is economically advantageous to be able to use the RGA as the systemâ?Ts total pressure gauge, rather than installing a total pressure gauge in addition to the RGA. The problem with using RGAs as total pressure gauges is that their sensitivity is affected by the mass of the gas they are detecting. These effects may be small for individual species of gas, but when the errors are added together in calculating the total pressure from the sum of the partial pressures, the total pressure measurement can become much less accurate than for gauges that measure total pressure only. This study is intended to find correction factors that can be applied to different gas species to make the RGA as accurate as any total pressure gauge. In this study, we use four Stanford Research Systems 100 AMU RGAs, an Ionivac IM-520 extractor gauge, an Ulvac AxTRAN gauge, and an MKS SRG SH-700 Spinning Rotor Gauge (SRG). First the SRG transfer standard is used to calibrate the extractor and AxTRAN gauges, by introducing various gases into the system, by direct comparison method. Then the RGA sensitivities for individual gas species are determined by comparing the partial pressure reading of the RGA with the extractor and AxTRAN gauge readings. Finally, a preselected gas mixture is introduced into the system, and the change in pressure reading on the extractor and AxTRAN are compared to the total pressure of the RGA with appropriate corrections to the various peaks of the RGA output. *This work was supported by U.S. Department of Energy Contract No. DE-AC05-84ER40150 and KATRIN International Collaboration at FZK in Germany.

10:40am **VT-TuM8 Calibration Systems Used for Calibrating Space Physics In-situ Particle Sensors*, M. Wüest,*** Astroglobo, Switzerland

Any measurement device needs to be calibrated to ensure that the signal output is in some known relation to the input. This is especially true for particle sensors sent into space. Those instruments can usually not be retrieved for recalibration in case questions about the validity of the measurements occur. Also, these in-situ space instruments are sometimes flown to locations where no other instrument has been before (e.g. Pluto). We will describe typical calibration systems for particle instruments for spacecraft such as plasma sensors, mass spectrometers, energetic neutral atom imagers or solid-state detector telescopes spanning the energy range from 0 eV to 10 MeV. We will touch upon selection for beam sources and beam monitors.

11:00am **VT-TuM9 Progress Towards User Oriented Vacuum Pressure Measurement*, M. Wuest,*** *R. Stocker,* INFICON Ltd., Liechtenstein

Since the beginning of vacuum measurements in the days of Torricelli, Pascal and von Guericke we have made a lot of progress in vacuum measurement. Measurement of total pressure in vacuum systems is characterized by an extremely large measurement range (> 14 decades) and the use of rather intransparent measurement principles such as heat conductivity of the gas, gas friction or ionization of the gas. This makes the measurement of the total pressure for the innocent user quite tricky as environmental parameters such as gas species, temperature, contamination or operating parameters must be considered. What efforts have been made in the past and what can be done in the future to provide the common user with simple to operate, accurate and reliable pressure gauges?

Exhibitor Workshop
Room Exhibit Hall C&D - Session EW-TuL

Vacuum Components and Measurement Optimization

Moderator: C. Bryson, Apparati, Inc.

12:00pm **EW-TuL1 Cold Cathode/Quartz Crystal Combination Gauge***, **E. Drubetsky**,* Televac*; B.R.F. Kendall,* Elvac Associates*; N. Matsumoto,* Tokyo Electronics Co., Ltd, Japan*; N. Ohsako,* VISTA Corporation*; H. Hojoh,* Vacuum Products Corp.

Different types of combination vacuum gauges have been introduced lately in the attempt to cover a wide range of measurements from atmosphere down to ultra high vacuum. In most cases they utilize one thermal conductivity type of gauge (usually Pirani) and one ionization gauge (hot or cold cathode). A combination gauge containing a quartz crystal and a cold cathode sensor is described.The miniature quartz oscillator in the shape of a tuning fork is located in a small isolated chamber of the cold cathode tube.This design allows expansion of the measurement range from 10@-9@ Torr to atmospheric pressure.Tests confirmed measurement error is within ±10% for pressure from 0.001 to 760 Torr. Repeatability data and durability against process gases are also discussed.

12:20pm **EW-TuL2 Seal Life Test of 300mm Hybrid Chamber in PVD Thermal Cycle Environment***, **J. Zhou**, M. Evans, J. Klein, J. Vargas, Y. Zhou, R. Schmieding, H. Gao, D. Paul, B. Stimson,* Applied Materials

Physical vapor deposition (PVD) is a key process in semiconductor wafer manufacturing. A new 300mm PVD chamber design consists of two pieces: an aluminum chamber body and a stainless steel bottom plate with a Viton O-ring seal. The reliability of the bottom seal is a concern, as elevated temperature exposure may cause the O-ring to fail by heat hardening, reducing equipment uptime. Thus, an accelerated test was designed to evaluate the O-ring lifetime before vacuum leakage. In commercial use, 300mm wafer diameter PVD chambers need to be heated for three hours at 80% lamp power about once a week. Tests were conducted with: 1) 100% lamp power during heating; 2) tight vacuum pass/fail criterion; 3) increased temperature in one of the test chambers than the default 96Â°C setting to look at worst case. Each thermal cycle consisted of three-hour heating and three-hour cooldown. After every 10 cycles the test chambers were cooled below 40Â°C to obtain the specified vacuum. Seal leakage was evaluated every 20 cycles using an in situ gas analyzer. Test chambers passed 520 thermal cycles without measurable vacuum degradation. Assuming 52 thermal cycles are equivalent to one year of seal life, the test chambers were demonstrated to have a "thermal equivalent" seal life of 10 years, which is much longer than the design goal of five years. The test results, together with post-test O-ring FTIR analysis, provide high confidence in O-ring reliability, and establish a methodology to evaluate PVD chamber seal life.

12:40pm **EW-TuL3 Robust System Identification and Optimized Tuning for Control of Evaporation Processes: Benchmark Study Results of Manufacturing Performance***, G. Reimann, B. Vattiat, **M. Gevelber**,* Cyber Materials, LLC*; J. Hildebrand, C. Hildebrand,* Maxtek, Inc.

Crystal monitors have been used for over 30 years to provide real-time control of evaporation sources in order to maintain a desired deposition rate. However, the performance of these systems is dependent on proper choice of controller gains. Review of a number of commercial operations has revealed that many controllers are mistuned and fail to compensate for large deposition rate variation. In many cases, poor controller tuning actually magnifies rate variations. These significant variations adversely impact coating quality, reduce yield, and limit throughput. In an evaporation system, the controller must be tuned to react to the dynamic response characteristics and disturbances typical of evaporation processes. The tuner will need to robustly deal with the process nonlinearities and variations that occur during a run. While a number of tuning approaches have been developed or suggested for controlling evaporation processes, none are optimized for the specific conditions observed in the processes, nor are they designed to handle the variety of conditions that typically occur. We present our work on a robust and automatic method for obtaining optimized controller tuning. The performance of the proposed tuning is evaluated under manufacturing conditions. We propose a two step process that first robustly identifies the system characteristics, and then applies an appropriate optimization scheme that selects controller gains based on the identified process characteristics. By robust, we mean that the identification process works despite all variations observed in practice including arcing, nonlinearities due to operating point dependency, and variations in system characteristics. In addition to describing the new robust and optimized controller tuning scheme, this paper reports our initial benchmark performance results of the new controller tuning system, as well as our analysis of system drift in several manufacturing systems.

1:00pm **EW-TuL4 Internet-Enabled Vacuum Training System***, R. Groom, **S. Hansen**,* MKS Instruments, Inc.*; Y.J. Lee, M. Moslehi,* Semizone, Inc.

Realizing that an understanding of vacuum and related process monitoring and control instrumentation is a key area for individuals who are technical workers in the semiconductor industry, MKS developed an integrated set of instructional literature and hardware for the teaching of vacuum and instrumentation practice. At the center is a table-top vacuum training system (VTS) which replicates the features and functions of a full-scale process tool. In 2004 MKS Instruments partnered with Semizone, Inc. to implement an Internet-enabled version of this vacuum training system. The system consists of most components found in a typical vacuum process tool including plasma chamber, high vacuum valve, throttling valve, mass flow controller, capacitance manometer, Pirani gauge, hot cathode ion gauge, RGA, and other components. Because the system was re-designed and built as an Internet enabled tool, all components (including components that are typically manually controlled) can be remotely actuated. The various sensors and actuators on the VTS interface with the equipment controller/server through adapters that convert legacy protocols into TCP/IP protocol. The equipment controller/server obtains the sensor readings and provides the control commands to the VTS. The equipment controller/server also communicates with the end user through client software using SOAP/XML protocol over a secure intranet or Internet connection. The client software provides graphical user interface and data analysis/interpretation tools. The remote access to the VTS is integrated with other Internet-based content including lecture modules, live video feeds, discussion forum, and online simulators.

1:20pm **EW-TuL5 CompuVac NT - A New Generation Vacuum System Design Tool***, **P.J. Klingner**,* Leybold Vacuum GmbH, Germany

Vacuum system design which meet the customer's requirements best is the goal of any vacuum equipment manufacturer. To achieve this the reliable modeling of the adequate system of pumps and conductances is a necessary and decisive precondition. Being in use for nearly two decades, Leybold's purpose-built software tool CompuVac has been successfully revised and transferred to the Windows@super TM@ environment now. The program helps to predict essential parameters as the effective pumping speed, pump down behaviour and power consumption reliably. Problems specific to a given vacuum system can be detected and purposively solved.

Biomaterial Interfaces
Room 311 - Session BI1-TuA
Sensors/Diagnostics

Moderator: M.J. Tarlov, National Institute of Standards and Technology

2:00pm **BI1-TuA1 Fluorescent Conjugated Polyelectrolytes: Superquenching, Biosensing and Biocidal Activity***, **D.G. Whitten**,* University of New Mexico **INVITED**

The talk will focus on the photophysics of fluorescent conjugated polyelectrolytes and their very high sensitivity (superquenching) to quenching by small molecules that can associate with the polymers and interact via energy or electron transfer. Superquenching occurs for the polymers in solution and also when they self-assemble on microspheres or nanoparticles. The application of superquenching to biosensing has provided a means for high sensitivity detection of enzyme activity, proteins and nucleic acid hybridization. It has also been found that these polymers have biocidal activity towards bacteria and bacterial spores. The origin of the light-induced biocidal activity will be discussed.

2:40pm **BI1-TuA3 Toward Improved Biosensors: Studies of Protein Immobilization on Polymerized Planar Supported Lipid Bilayers***, **J. Joubert**, E.H. Elandaloussi, S.S. Saavedra,* University of Arizona

Planar supported phospholipid bilayers maintain high resistance to nonspecific protein adsorption, which is a useful attribute for biosensor surfaces. However, their instability to drying is a factor reducing their commercial implementation. By crosslinking polymerizable lipid monomers (e.g., bis-sorbylphosphatidylcholine, bis-SorbPC) bilayer stability can be increased while maintaining biofouling (i.e., nonspecific protein adsorption) resistance. Further, the properties of this poly(bis-SorbPC) platform can be modified to study nonspecific and specific interactions with proteins for biosensing applications. One modification for studying nonspecific interactions involves adding various percentages and types of nonpolymerizable lipid to the bilayer before polymerization and drying to introduce a varying number and size of defect sites with differing polarities (hydrophobic for exposed lower lipid leaflet and hydrophilic for exposed glass) in a controlled manner. Studies of nonspecific protein binding to this variety of defects in these bilayers can aid in understanding fouling and subsequent failure of biosensors. Another set of modifications for analyzing specific protein interactions is aimed at immobilizing analyte-specific receptor proteins onto the bilayer and analyzing the degree to which sensing activity is retained. These modifications include doping into the bilayer a polymerizable lipid with a reactive (e.g., primary amine) headgroup for protein receptor attachment or microcontact printing the protein receptor onto the polymerized bilayer. This talk will discuss development of such methodologies to attach proteins to poly(lipid) bilayers to study protein-lipid and protein-protein interactions on such surfaces.

3:00pm **BI1-TuA4 Gallium Nitride-based BioFETs for Label-free Biosensing***, **K. McCoy**,* University of Florida*; J.C. Sullivan, J.C. Culbertson, E. Snow,* Naval Research Laboratory*; S.J. Pearton,* University of Florida*; L.J. Whitman,* Naval Research Laboratory

Biologically modified field effect transistors (BioFETs) have the potential to directly detect biochemical interactions in aqueous solutions for a myriad of applications. In order for these devices to be useful, they must satisfy three major criteria. The bioFET must be stable in aqueous solutions across a range of pH and salt concentrations, be sensitive to biochemical interactions on the surface of the device, and be able to probe specific biochemical interactions. BioFETs that we are developing based on AlGaN/GaN quantum well devices can potentially satisfy all of these requirements. These charge-sensitive devices are being functionalized with receptors to stochastically sense the binding of target molecules in aqueous samples. The sensing is based on device geometries whereby the stochastic binding of individual biomolecules above a device will cause a change in conductance. It has already been demonstrated that these AlGaN/GaN quantum well devices can sense small changes in pH of electrolyte solutions. It is our goal to functionalize the surface in such a manner that the sensitivity of the device is not severely reduced. We are evaluating two reaction schemes to accomplish this task. The first involves modifying the surface with a SAM, then attaching a polymer to that SAM which can couple to biological probes. The second method employs a proprietary scheme to functionalize the surface with a layer of avidin that can then be coupled to biotinylated probes. The reaction schemes have been characterized in both UHV (XPS) and solution (cyclic voltammetry, fluorescence microscopy). The effect of these schemes on the electrical properties of the devices will be discussed, along with our progress toward determining the ultimate sensitivity of this biosensor system.

3:20pm **BI1-TuA5 Increasing Immunosensor Responses: from Antibody Fragments and 3D Substrates to Functionalized Nanoparticles***, **K. Bonroy**,* IMEC and K.U. Leuven, Belgium*; F. Frederix,* IMEC, Belgium*; P. Cliquet,* R.U. Gent, Belgium*; G. Reekmans, H. Jans, T. Ghoos, R. De Palma, W. Laureyn,* IMEC, Belgium*; B. Goddeeris,* K.U. Leuven and R.U. Gent, Belgium*; P. Declerck,* K.U. Leuven, Belgium*; G. Borghs,* IMEC, Belgium

Researchers are continuously seeking for new transduction principles and biosensor interfaces. Both the transducer and biochemical interface contribute to the sensor signal. However, over the years it became clear that a lot of these approaches lack sensitivity for some applications. In this paper we report on several modifications at the (bio)chemical interface in order to increase/tune the immunosensor signal. Two important routes were investigated; the increase of the amount of active/well-oriented receptormolecules on the surface and the use of functional nanoparticles for signal amplification. In this paper we present some of our approaches to control the amount of immobilized molecules and to mitigate non specific adsorption of proteins. Different mixed thiol SAMs, indirect assay formats, immobilization methods, 3D nanoparticle films, 3D porous gold surfaces, and size-reduced receptormolecules such as ScFvs and Fab antibody fragments were optimized, characterized and their influences on the sensor response were evaluated. We will show that some of these modifications at the level of the interface can generate a considerable increase in the response of immunosensors such as SPR, QCM and electrochemical sensors. In addition, we also optimized some of the above-mentioned enhancement approaches towards one application i.e. antibiotic detection. Therefore, a new antibiotic modified disulfide was synthesized and evaluated on gold substrates and nanoparticles. The characterization and optimization was performed using XPS, SPR, IR, CA, CV and TEM. The antibiotic tailored surfaces and nanoparticles were also evaluated in the final biosensing application. In conclusion, we will show that (bio)chemical modifications of the immunosensor interface can be used to manipulate and control the final sensor signal. In addition, we will show that interface modifications could offer a platform from which application-specific sensitivity problems can partially be addressed.

3:40pm **BI1-TuA6 Fluidic Force Discrimination Assays in Complex Media***, **S.P. Mulvaney**, A.A. Glaser, M. Malito, C.R. Tamanaha, J.C. Rife, L.J. Whitman,* Naval Research Laboratory

We are developing a highly sensitive and selective biosensor system that uses giant magnetoresistive sensors arrayed in a Bead ARray Counter (BARC) microchip to directly detect magnetic microbead labels. The beads are used both to label biorecognition events in a binding assay and to reduce background through a process known as fluidic force discrimination (FFD). FFD is a controlled bead removal procedure that leverages the strength of biomolecular recognition against fluidic forces to selectively remove nonspecifically bound beads and beads labeling nonspecifically bound analyte. FFD not only reduces the background label density, thereby improving the analytical sensitivity of the binding assay, but also lowers the occurrence of false positives. Highly sensitive DNA assays (<10 fM) and immunoassays (<1 ng/mL) have been demonstrated in less than 30 minutes at room temperature, without amplification or concentration steps (i.e. PCR). Successful assays have also been run in serum, plasma, whole blood, and complex environmental matrices. We'll discuss mitigation steps (i.e. addition of chelating agents, filtration, etc.) required to achieve detection in complex media as well the overall impact on detection levels. We'll also examine the ability to minimize sample handling by incorporating simple processing capabilities into the microfluidics cartridge. @FootnoteText@ S.P.M., A.A.G., and M.M. are employees of Nova Research Inc., Alexandria, Va.

Biomaterial Interfaces
Room 312 - Session BI2-TuA
Surface Modification

Moderator: A. Chilkoti, Duke University

2:00pm **BI2-TuA1 Dynamic Ellipsometric Studies of Protein Adsorption to Modified Chitosan Surfaces***, **S. Sarkar**, L.G. Castro, D.W. Thompson, J.A. Woollam, A. Subramanian,* University of Nebraska, Lincoln

Protein adsorption is a ubiquitous phenomenon whose effects are widespread and observable in fields as diverse as biofouling, molecular recognition and metabolic pathway activation (biocompatibility) and even qualitative and quantitative detection methods (ELISA). Protein interaction with materials and at interfaces is an area of ongoing study; however, little is understood of the immediate response of proteins to an exposed surface. Chemically modified chitosan films were used to investigate the adsorption of human serum albumin (HSA), immunoglobulin G, and fibrinogen. Diepoxides were reacted with amine groups present on chitosan and then five atomic geometries (n-butyl amine, 2-(t-Butylamino)ethanol, n-octyl amine, 2,4,6 Tris(dimthylaminomethyl) and t-butyl amine) and an anti-HSA molecule were attached to free epoxide ends to create surfaces preferential to albumin adsorption. Dynamic ellipsometric studies were carried out on the resulting surfaces to investigate protein adsorption phenomena. We have been successful in observing real time protein adsorption. In most cases protein adsorption had reached a saturation point after one-hour with the highest rate of adsorption occurring in the first ten minutes.

2:40pm **BI2-TuA3 The Generation of Protonated Amine Groups in Plasma Co-Polymers of Acrylic Acid and Allylamine for the Co-Culture of Keratinocytes and Melanocytes***, **A.J. Beck**, P. Eves,* University of Sheffield, UK*; J.D. Whittle,* Plasso Technology Ltd, UK*; N.A. Bullett,* Celltran Ltd, UK*; S. Mac Neil, S.L. McArthur, A.G. Shard,* University of Sheffield, UK

Plasma polymers prepared from acrylic acid, allylamine and mixtures of the two strongly interacting vapors were characterized using X-ray photoelectron spectroscopy (XPS) and near edge X-ray fine structure (NEXAFS). Plasma polymers prepared from pure acrylic acid and allylamine contained groups retained from the monomer with additional groups formed in the plasma. For the plasma copolymers, the XPS N 1s data and NEXAFS N k-edge provided evidence of protonated amines. The mixture of monomer vapors, in the absence of a plasma, consists of acrylic acid, allylamine and the product of their reaction: allylammonium acrylate salt. More protonated amines were detected in plasma copolymers prepared at low powers suggesting that they were largely retained from the monomer mixture rather than being formed in the plasma. The protonated amines in the monomer mixture undergo less dehydrogenation to nitrile groups in the plasma than the amines from the pure allylamine. This novel use of protecting groups for amines in low power plasmas has the potential to be extended to other desirable groups which tend to be diminished due to fragmentation even in very low power systems. We have demonstrated that plasma co-polymers of acrylic acid and allylamine contain protonated amine groups with carboxylates as the counter anion. It is postulated that such zwitterionic plasma polymers will have interesting surface charge properties in aqueous solution and it may be possible to control the isoelectric point of the surface by varying the plasma conditions and ratio of allylamine to acrylic acid vapors. These surfaces have been shown to facilitate co-culture of keratinocytes and melanocytes.

3:00pm **BI2-TuA4 Pulsed RF Plasma Polymerisation of N-isopropylacrylamide (NIPAAm)***, **R. Talib**, A.G. Shard, S.L. McArthur,* University of Sheffield, UK

There is a growing interest in the development of responsive polymer coatings for applications as diverse as tissue engineering and microfluidic devices. Plasma polymerization affords a convenient, one step route to generate such coatings. Previous studies have shown that continuous wave (CW) plasma polymerization of N-isopropylacrylamide (NIPAAm) is able to produce thermally responsive coatings on a variety of substrates. These CW studies have demonstrated that control of the deposition power and temperature is critical for the retention of functionality, but that too little power or too lower temperature will result in unstable coatings. In this study we investigate the use of pulsed power cycles as a means for both improving coating stability and controlling the thermal response of the coatings. We have investigated the influence of power, on- and off-times and reactor temperature on the coating chemistry, stability and thermal response. The role of the plasma parameters has been monitored using a capacitive probe. The probe enables accurate measurement of the duty cycle and clearly demonstrates that in certain regimes both the power and ratio of on/off time set by the pulse generator can result in significant delays in the striking of the plasma. In some instances, we demonstrate that the plasma actually fails to ignite during the majority of individual pulses. Accurate measurement of duty cycles enables direct comparison of coatings produced under pulsed power with those produces with equivalent CW powers. X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS) and captive bubble have been used to measure the resulting coating properties and compare the mechanisms of NIPAAm polymerization under CW and pulsed plasma conditions.

3:20pm **BI2-TuA5 Using Plasma Deposits to Promote Cell Population of the Porous Interior of 3D Tissue Engineering Scaffolds***, J.J.A. Barry, M.M.C.G. Silva, K.M. Shakesheff, S.M. Howdle, **M.R. Alexander**,* University of Nottingham, UK

Cell attachment and proliferation on poly(D,L-lactic acid) (PLA) tissue engineering scaffolds is low, this is generally regarded to be due to the hydrophobicity of the polymer surface. This study reports the first successful deposition of allyl amine plasma polymer throughout the porous network of a 3D scaffold to improve cell adhesion. This is compared and contrasted with the plasma grafting of allyl amine to the PLA. XPS analysis of sectioned scaffolds is used to demonstrate the penetration of nitrogen species to the inner surfaces. The nitrogen concentration at the exterior and interior scaffold surface was greater for the plasma deposits than the grafted surfaces. The variation in nitrogen concentration indicated a variation in thickness through the scaffold due to diffusion limited deposition in the interior pores. The chemistry was characterised using high resolution C1s and N1s core level with reference to literature NEXAFS and derivatisation studies. In vitro evaluation of biocompatibility was carried out by studying 3T3 fibroblast attachment, morphology and metabolic activity on the scaffolds. Cell activity and attachment was found to be greater for the plasma deposits than the plasma grafted PLA scaffolds and greater for both than the as-fabricated PDLLA scaffolds. It is concluded that plasma deposition is a viable method of increasing cell attachment throughout porous PLA and other scaffolds without changing the bulk characteristics of the polymer.

3:40pm **BI2-TuA6 Designing Interfaces for Biomolecular Interactions using Plasma Polymerization Techniques***, **R. Foerch**,* Max Planck Institute for Polymer Research, Germany

Recent advances in the synthesis and characterisation of plasma polymerized thin organic coatings has enabled new insights into the design of interfaces for specific interactions with biological molecules. Optical techniques such as surface plasmon resonance and waveguide mode spectroscopy have been used to monitor in real-time the reactions of proteins, antibodies and DNA at the interface of different plasma polymerised films. Combining these techniques with AFM, FTIR and XPS analysis has demonstrated a tremendous flexibility in surface design, plasma polymer structure and surface reactivity. The chemical composition, the macromolecular structure and the ability to form a 3-dimensional interface open up new concepts for the design of biomaterial surfaces. The interactions of proteins, antibodies and DNA can be correlated to plasma deposition conditions and subsequently the chemical and physical properties of the deposited layers.

Electronic Materials and Processing
Room 310 - Session EM+MI-TuA

Spin Injection

Moderator: C.J. Palmstrom, University of Minnesota

2:40pm **EM+MI-TuA3 Characterization of Mn-based Contacts on GaAs***, **J.L. Hilton**[1], B.D. Schultz, S. McKernan, C. Adelmann, X. Lou, P.A. Crowell, C.J. Palmstrom,* University of Minnesota

Mn-based ferromagnetic materials, such as binary metals, Heusler alloys, diluted magnetic semiconductors, and digital alloys, are potentially useful as epitaxial spin injection contacts in GaAs-based spintronic devices. Defects and solid-state reactions at a ferromagnet/semiconductor interface have a significant influence on the spin injection efficiency of spintronic devices. Consequently, a detailed understanding of the interfacial interactions of Mn and Mn-based materials with GaAs is needed. In order to understand the thermodynamic phase behavior of the Mn-Ga-As ternary system, thin film Mn/GaAs structures were grown using molecular beam epitaxy. RHEED, LEED, STM, XPS, RBS, XRD, and cross-sectional TEM were used to characterize the Mn/GaAs interfacial reactions. These reactions initially resulted in the formation of a two-phase region of tetragonal Mn@sub 2@As and tetragonal @delta@-MnGa, with an average composition of Mn@sub 0.6@Ga@sub 0.2@As@sub 0.2@. The two phases formed an epitaxial lamellar layer on the GaAs substrate with Mn@sub 2@As(001) and @delta@-MnGa(001) // GaAs(001). Higher temperature anneals resulted in the dissociation of the Mn@sub 0.6@Ga@sub 0.2@As@sub 0.2@ region into a @delta@-MnGa layer near the sample surface and a Mn@sub 2@As layer near the GaAs substrate. Anneals of @delta@-MnGa films on GaAs suggest that @delta@-MnGa is

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[1] **Falicov Student Award Finalist**

thermodynamically stable in contact with GaAs over a narrow compositional range up to at least 400°C. For more Ga-rich Mn@sub 1-x@Ga@sub x@ films, no evidence of interfacial reactions with GaAs was observed, but there were significant structural changes within the film. Stable @delta@-MnGa films are especially desirable for use in spintronic devices due to their inherent perpendicular magnetization. Spin injection measurements utilizing @delta@-MnGa contacts on GaAs-based spin-LEDs will be presented. Supported by ARO, ONR, DARPA, NSF, and AFOSR.

3:00pm **EM+MI-TuA4 Interface Structure and Spin Injection Efficiency in a Ferromagnetic/Semiconductor Spin-LED***, **A.T. Hanbicki**, G. Kioseoglou, R. Goswami, T.J. Zega, O.M.J. van 't Erve, C.H. Li, R.M. Stroud, G. Spanos, B.T. Jonker,* Naval Research Laboratory

Considerable effort has been made to incorporate ferromagnetic metals into semiconductor spintronic devices. The nature of the interface between a magnetic contact and a semiconductor is expected to influence the spin-injection efficiency. Indeed, we have discovered interface effects play a role in the spin-injection efficiency for an all-semiconductor system.@footnote 1@ Recently we demonstrated robust spin injection from Fe into an AlGaAs/GaAs spin-LED. With this system, we have successfully injected spin polarized electrons with an electron spin polarization of 32% in the GaAs quantum well (QW).@footnote 2@ To correlate the interface structure with the observed QW polarization, we have characterized our Fe/AlGaAs contacts using high-resolution transmission electron microscopy (HRTEM), electron energy-loss spectroscopy, and high-angle annular-dark-field (HAADF) imaging. HRTEM together with HAADF imaging provides compositional information that can also be used to determine the interfacial character. We have studied several samples with different detector heterostructures. Optimized annealing can improve the measured spin polarization, therefore for each sample several pieces were annealed to generate a systematic dataset. Enhancement in polarization is seen with anneals as low as 175°C, and the maximum increase in polarization occurs for anneals above 200°C. Measured spin polarizations increase by 8 to 10%, independent of the starting value. Preliminary results reveal a correlation between the GaAs QW spin polarization and the thickness of the Fe/AlGaAs interface. As the interface thickness increases from 0.5 to 0.9 nm, the measured polarization decreases from 27% to 18%. There are also indications that the Fe film is affected by annealing and implications toward spin injection will be discussed. This work was supported by the DARPA SpinS program and ONR. @FootnoteText@ @footnote 1@R.M. Stroud, et al, PRL 89 (2002)@footnote 2@A.T. Hanbicki, et al, APL 82 (2003).

3:20pm **EM+MI-TuA5 Gate-Controlled Electron Spin Transport for Nonmagnetic Spintronics***, **K.C. Hall**,* Dalhousie University, Canada*; K. Gundogdu, J.L. Hicks, A.N. Kocbay, M.E. Flatte, T.F. Boggess,* University of Iowa*; K. Holabird, A. Hunter, D.H. Chow, J.J. Zinck,* HRL Laboratories, LLC **INVITED**

The prospect of novel high-performance spin-based semiconductor technologies has lead to new research in spintronics, in which the fields of electronics, photonics, and magnetics merge with the promise of applications in ultra-low-power logic architectures, non-volatile reprogrammable gate arrays, and optoelectronic technologies. Innovation in these areas requires the development of efficient methods for spin injection and manipulation in semiconductor materials. Spintronic device architectures that do not require external magnetic fields or magnetic contacts are especially attractive as they would provide seamless integration with the materials and processing techniques of existing semiconductor devices, while avoiding undesirable stray magnetic fields that may hinder device performance. We show that highly spin-polarized electron spin injection may be achieved in side-gated resonant interband tunnel diodes (RITDs) based on nonmagnetic (110) InAs/GaSb/AlSb heterostructures.@footnote 1@ Due to the strong spin-orbit effects in this system, electron spin splittings due to bulk inversion asymmetry approach 40 meV, permitting operation of the spin-RITD at practical temperatures. A nonmagnetic spin field effect transistor incorporating RITD contacts and gate-controlled spin relaxation will be described, along with our recent experiments demonstrating low-threshold spin lifetime switching in this device.@footnote 2@@FootnoteText@This research is supported by DARPA MDA972-01-C-0002, DARPA/ARO DAAD19-01-1-0490, NSF ECS 03-22021, and NSERC. @footnote 1@K.C. Hall et al., Appl. Phys. Lett. 83, 2937 (2003); @footnote 2@K.C. Hall et al., to be published in Appl. Phys. Lett. (2005).

Electronic Materials and Processing
Room 309 - Session EM-TuA

Growth and Characterization of ZnO

Moderator: T.J. Coutts, National Renewable Energy Laboratory

2:00pm **EM-TuA1 Expanding Thermal Plasma Deposited ZnO Films: Effect of Al Doping on the Thin Film Growth***, **I. Volintiru**, M. Creatore,* Eindhoven University of Technology, The Netherlands*; J.L. Linden,* TNO Science and Industry, The Netherlands*; M.C.M. Van De Sanden,* Eindhoven University of Technology, The Netherlands

Zinc oxide (ZnO) films have been extensively studied in the past decade due to their advantages over other transparent conductive oxides (TCOs) such as large exciton binding energy, possibility of wet chemical etching, non-toxic precursors, and low-cost production. For specific applications, a good control of the ZnO film electrical and optical properties, as well as the surface morphology (e.g. high roughness needed for light trapping within solar cells) is necessary. In this work, both undoped and Al-doped ZnO films are deposited on crystalline Si and glass substrates using an argon-fed expanding thermal plasma in which oxygen, diethylzinc (and trimethylaluminium for Al doping) are admixed downstream. The in-situ real-time spectroscopic ellipsometry (SE) and atomic force microscopy (AFM) performed on undoped ZnO point out towards a linear roughness development (about 10% of the film thickness) starting from 10 nm film thickness. Moreover, both AFM and X-ray diffraction (XRD) measurements indicate a polycrystalline film growth above 10 nm. The influence of Al doping on the ZnO film electro-optical properties, surface morphology and crystallinity obtained from Hall, in-situ SE, AFM and XRD, respectively, will be presented.

2:20pm **EM-TuA2 Carbon Passivation Effect in ZnO Thin Film***, **X. Li**, S. Asher, C.L. Perkins, B.M. Keyes,* National Renewable Energy Laboratory*; S. Limpijumnong,* Suranaree University of Technology, Thailand*; S.B. Zhang, S.-H. Wei, T.J. Coutts, R. Noufi,* National Renewable Energy Laboratory

Carbon impurity is commonly found in thin films fabricated by metal-organic chemical vapor deposition (MOCVD). The role of carbon in undoped and nitrogen-doped ZnO thin films was studied experimentally and theoretically to understand the possible compensation effect of carbon. ZnO thin films were fabricated by low-pressure MOCVD using diethylzinc and oxygen precursors. Nitrogen doping was achieved with nitric oxide (NO) gas. High levels of carbon incorporation were observed in the ZnO film, especially for nitrogen-doped ZnO film. Fourier transform infrared (FTIR) spectroscopy observed the possible C-H@sub x@ (x=1, 2, and 3) defect complex in the unintentionally doped ZnO film. Both FTIR and X-ray photoelectron spectroscopy observed the possible N-C defect complex in the nitrogen-doped ZnO. The first-principles calculations predict that the N-C defect complex is 1+ charge state. Therefore, the existence of carbon and the N-C defect complex could compensate the nitrogen acceptor species.

3:20pm **EM-TuA5 Direct Formation of Nanoporous ZnO Networks by MBE***, **S.M. Durbin**, W.C.T. Lee, R.P. Millane, R.J. Reeves,* University of Canterbury, New Zealand*; Z. Liu, S. Ringer,* University of Sydney, Australia*; F. Bertram,* Otto-von-Guericke-University Magdeburg, Germany

Porous semiconductors have captured significant attention in the past decade, both as a result of visible luminescence from silicon structures and due to the potential for creating surface-active devices such as gas sensors. Porous networks of these materials are generally formed in conjunction with some form of anodic etching procedure, although some arc processing has been reported as well. In contrast, we have observed the direct formation of large-scale multi-level nanoporous ZnO networks grown using an RF plasma-assisted molecular beam epitaxy (RF-PAMBE) technique without the need for etching or other postprocessing. Elemental Zn was evaporated using a standard effusion cell, and active oxygen was supplied using an Oxford MDP21 plasma source with alumina components in the plasma chamber. In-situ reflection high-energy electron diffraction exhibited patterns consistent with c-axis oriented single crystal growth on the GaN/sapphire template. Initial estimates indicate a porosity of at least 20% based on analysis of field emission scanning electron microscopy images, which also show feature sizes on the order of tens of nanometres and pores of approximately 100 nm in diameter. Cross-sectional transmission electron microscopy confirms the presence of a porous network on top of a 20 nm thick continuous ZnO layer. Low temperature photoluminescence reveals a broad feature near the bandedge of ZnO, which is near the short wavelength limit of the measurement apparatus. The driving mechanism underlying the formation of the nanoporous layer is unclear, but may be related to preferentially-oriented surface features formed on the GaN buffer layer. This work is supported in part by the MacDiarmid Institute for Advanced Materials and Nanotechnology, and the University of Canterbury.

3:40pm **EM-TuA6 STM Study of Gold Nanoparticles on ZnO Film Annealed at Different Temperature***, **R.S. Aga**, A. Ueda, W.E. Collins, R. Mu,* Fisk University

ZnO nanowires are promising for photovoltaic applications. In addition, ZnO film may also be used as a transparent electrode. Direct growth of ZnO nanowires on ZnO film via gold nanoparticles may then provide a better transport of photogenerated charges from the nanowire to the electrode. Thus, it is important to understand the effect of thermal treatment on the microstructure and electronic properties of gold nanoparticles deposited on ZnO film. In this work, we use STM to study spin-coated gold nanopaticles on ZnO films annealed at different temperatures. The films were grown by electron beam deposition. Our results may be useful in optimizing nanowire properties as well as improving nanowire connectivity to the electrode.

Magnetic Interfaces and Nanostructures
Room 204 - Session MI-TuA

Magnetization Dynamics

Moderator: E. Nowak, University of Delaware

2:00pm **MI-TuA1 All Optical Pump/Probe Spectroscopy from Coherent Spin Waves in Exchange Bias Systems***, **B. Beschoten**, A. Tillmanns, S. Oertker, G. Guentherodt,* RWTH Aachen, Germany*; I.K. Schuller,* UC San Diego **INVITED**

Time-resolved Kerr rotation is used to generate and to probe coherent spin waves in exchange biased ferro-/antiferromagnetic bilayer films of Fe/MnF@sub 2@. In time-resolved Kerr rotation, an ultrafast laser pump pulse generates an unidirectional anisotropy field pulse which triggers coherent precession of the magnetization in the ferromagnetic layer. This coherent precession can be monitored by a time-delayed laser probe pulse yielding a quantitative method to study local magnetic anisotropies, ultrafast switching and damping phenomena. This time-resolved all-optical technique is combined with static vector MOKE measurements, which allow to link static magnetization reversal processes, such as coherent rotation of the magnetization vector or domain wall nucleation and propagation, with the precessional switching dynamics at all magnetic fields during magnetization reversal. Work supported by DFG/SPP 1133 and by European Community's Human Potential Program/NEXBIAS. Work at UCSD supported by US-DOE and by AFOSR.

2:40pm **MI-TuA3 Current-Driven Magnetization Dynamics: Domain Wall Motion and Thermal Effects***, **S. Zhang**, J. He, Z. Li,* University of Missouri-Columbia **INVITED**

The spin current induced spin torque has been written in several different forms, depending on materials as well as geometrical arrangements. We outline the key features of those various forms. Here we concentrate on two interesting issues: the effect of spin torques on the thermal assited magnetization reversal and the domain wall depinning by a spin torque. In the first case, we have demonstrated that a stochastic Fokker-Planck equation which explicitly includes the spin torque can be established and solved when the current is not too large, and thus we are able to predict finite temperature current-driven magnetization dynamics. In the second case, we investigate the effect of currents on geometrically confined domain walls. In particular, we construct domain wall pinning/depinning phase diagrams in terms of the applied magnetic field and the current. Our results agree with existing experimental data.

3:20pm **MI-TuA5 Propagation and Tunneling of Spin Waves through a Magnetic Field Inhomogeneity***, **B. Hillebrands,*** University of Kaiserslautern, Germany*; S.O. Demokritov,* University of Muenster, Germany*; A.A. Serga,* University of Kaiserslautern, Germany*; V.E. Demidov,* University of Muenster, Germany*; M.P. Kostylev,* University of Kaiserslautern, Germany*; A.N. Slavin,* Oakland University **INVITED**

We show experimentally and by numerical simulation, that spin waves propagating in a magnetic film can pass through a region of a magnetic field inhomogeneity, or, alternatively, can be reflected by the region depending on the sign of the inhomogeneous field contribution. If the reflecting region is narrow enough, spin wave tunneling may take place. We investigate the tunneling mechanism and demonstrate that it has a magnetic dipole origin. While travelling through a region of inhomogeneous field, spin waves undergo a phase shift. We show experimental evidence and we discuss that this can be used for designing phase shifters and spin-wave logic elements.

Manufacturing Science and Technology
Room 207 - Session MS-TuA

Advanced Manufacturing Processes for Silicon Devices

Moderator: A.C. Diebold, SEMATECH

2:00pm **MS-TuA1 Magnetoresistive Random Access Memory - Manufacturing Challenges***, **G.W. Grynkewich**, B. Butcher, J. Chan, W. Feil, G. Kerszykowski, K. Kyler, J. Martin, J. Molla, K. Nagel, J. Ren, K. Smith, J.-J. Sun, R. Williams,* Freescale Semiconductor, Inc. **INVITED**

Magnetoresistive random access memory (MRAM) combines a magnetic tunnel junction (MTJ) with standard silicon-based CMOS to provide a unique combination of high speed read and write, non-volatility, and unlimited read and write endurance. We have produced the world's first commercially viable MRAM circuits. After a brief description of the fundamentals of an MTJ-based MRAM, we will describe the manufacturing challenges associated with the volume production of high performance MRAM parts. These include: contamination control, bit patterning, achieving and maintaining uniformity of both very thin magnetic films and the tunnel barrier, formation of cladded programming lines, and processing very thin interlayer dielectrics.

2:40pm **MS-TuA3 Controlling Ultrashallow Junction Formation through Surface Chemistry***, **E.G. Seebauer**, K. Dev, C.T.M. Kwok, R.D. Braatz,* University of Illinois at Urbana-Champaign

Forming extremely shallow pn junctions with very low electrical resistance is becoming an insurmountable stumbling block to the continued scaling of microelectronic device performance according to Moore's Law. We have developed a technology based on surface chemistry that holds great promise for simultaneously reducing junction depth and increasing activation for dopants implanted into silicon. The approach uses the surface as a large controllable "sink" that removes Si interstitials selectively over dopant interstitials. We have discovered a new way to employ adsorption at the surface for this task: adjusting the intrinsic loss rate of interstitials to the surface. We control the interstitial loss rate to the surface by saturating dangling bonds using adsorbed nitrogen (introduced as ammonia) before implantation or the subsequent annealing step. To demonstrate such effects, we have measured SIMS profiles of isotopically labeled Si (mass 30) implanted into a Si host lattice depleted in this isotope, The annealed profiles with an atomically clean surface change relatively little from the as-implanted profile, while the profiles with adsorbed N change much more. We have quantified the loss rate of interstitials at the surface by measuring the annihilation probability, which varies from about 0.05 on atomically clean Si(100) to about 0.0008 with only 1% of a monolayer of adsorbed N.

3:00pm **MS-TuA4 Investigation of Boron Penetration through Poly Silicon Films***, **X.-D. Wang**, W. Fan, S. Phillips, J. Parker, S. Schauer,* Freescale Semiconductor

Poly-Si is the most commonly used gate material in modern VLSI fabrication. It is also widely used as mask layer for dopant implantation. Such a process has the advantage of reducing lithography steps, however, it requires tight control on film property in order to effectively block undesired implantation through the film to the substrate silicon. In this paper, we investigate an implant issue related to boron penetration through the poly-Si film. Plan view scanning capacitance microscopy (SCM) analysis was performed to examine MOSFET devices which failed due to short channel. SCM images directly revealed undesired boron penetration in CMOS channel region to be the root cause of the failure. It was found that the yield was related to poly-Si deposition conditions. Multiple analytical techniques, including SCM, second ion mass spectroscopy (SIMS) and, transmission electron microscopy (TEM) were used to characterize the severity of boron penetration as function of film deposition conditions, especially the deposition temperature. By correlating to TEM analysis, it was found that the boron penetration is closely related to the crystalline properties of the film and optimal film growth parameters were obtained.

3:20pm **MS-TuA5 Investigation of Low-k Dielectric Etching using Groovy ICP Plasma Source**, *A. Kelly*, ***G.K. Vinogradov***, FOI Corporation, Japan

Plasma etching of low-k dielectric materials, such as porous materials is presenting significant challenges to their introduction in copper dual damascene device production. Plasma damage is implicated in poor retention of low-k properties. We investigated plasma damage using a narrow gap inductive plasma source, Groovy ICP. Specially developed for 300mm low-k dielectric etching, it has three independently controllable highly efficient RF coils immersed in separate grooves machined in a planar roof. Each groove generates its own plasma toroid, both radial plasma density and chemical uniformity can be optimized. We investigated sidewall damage in dual damascene stack structures over a wide pressure range for porous low-k dielectrics. Only under conditions of low pressure, 5-10mTorr and low ion energy can sidewall damage be eliminated. With separate wafer bias control of ion energy, we can distinguish between ion and radical effects on sidewall damage of low k materials. Damage is by radical attack penetrating into the sidewall; therefore low-pressure ion dominant conditions are needed. Also low ion energy is needed as high ion energy conditions can sputter damage sidewalls. Groovy ICP is capable of achieving these conditions in a narrow gap, typical for low residence time oxide etchers. This shows its unique applicability for low-k dielectric etching including oxide layers.

Nanometer-Scale Science and Technology
Room 210 - Session NS+BI-TuA

Molecular and Biological Applications of Nanostructures

Moderator: M.C. Hersam, Northwestern University

2:00pm **NS+BI-TuA1 Nano-Patterned Surfaces Induce Bio-Molecules Oriented Immobilization**, ***A. Valsesia***, *P. Colpo, T. Meziani, P. Lisboa,* EC-JRC-IHCP Italy*; M. Lejeune, F. Rossi,* EC-JRC-IHCP Italy, Italy

The immobilization of biomolecules in domains with the typical size of the nano-meter or few tenth of nano-meters is one of the most challenging issues of the actual research in the field of biosensors and biochips. In particular the ability to create nanopatterned bio-active surfaces should be addressed to improve the performances of biosensing devices and to study new fundamental problems. From the technological point of view the nano-patterned surfaces can improve or modulate the absorption of proteins, minimize their non-specific absorption, increase the active surface density. In the last few years nano-soft lithography, dip-pen lithography, nano-fountain pen lithography and colloidal lithography were able to produce nano-patterned surfaces with fouling-antifouling contrast. The selective immobilization of the biomolecules on the fouling regions was demonstrated as well as the reduction of the nonspecific absorption in the antifouling matrix. In this work we developed a nano-patterning method which combines the spontaneous formation of molecular monolayers (SAM) and plasma based colloidal lithography. By this approach we have shown that the nano-patterning resolution is not limited in principle and can be accurately controlled by the plasma processing parameters. The techniques was employed for the creation of chemical nano-patterned surfaces with 100 nm motives with a hexagonal 2-D crystalline structure, characterized by COOH terminated SAM nano-spots in a CH3 terminated thiols matrix. By combining the information arising from the different characterization techniques, it was possible to demonstrate the creation of a chemical contrast with a resolution of 100 nm, without a meaningful change in the morphological properties of the surface. An effective orientation of the biomolecules immobilized on these nano-patterned surfaces was demonstrated by AFM measurements and confirmed using an ELISA antibody immobilization protocol.

2:20pm **NS+BI-TuA2 Surface Nanopatterning for the Control of Cell Behavior**, ***C.M. Dekeyser***, *J. Marchand-Brynaert, A.M. Jonas, Ch.C. Dupont-Gillain, P.G. Rouxhet,* Université Catholique de Louvain, Belgium

Cell adhesion is mediated by proteins of the extracellular matrix, called adhesion proteins. RGD (arginine-glycine-aspartic acid) is the most widely spread peptide sequence responsible for these recognition events. It has been shown that a surface covered by adhesion proteins or grafted with the RGD sequence can induce different cell behaviors, depending on the distribution of the ligands. The aim of the work is to get a better insight into the influence on cell behavior of the distribution of ligands at the nanometer scale. This involves four aspects: creating a nanostructured surface, grafting a RGD ligand or adsorbing an adhesion protein according to defined motifs, passivating the rest of the surface with respect to protein adsorption and evaluating the cell behavior. The nanopatterns are created by means of electron-beam lithography. The challenge here is to draw small motifs (100 nm) on an area (500*500 µm@super 2@), large enough to allow cell adhesion to be studied. This was realized by juxtaposition of patterns (143*143 µm@super 2@) on which electron-beam lithography allowed continuous and regular lines to be drawn. In order to minimize non specific protein adsorption, the passivation of the surface is realized by self-assembly of oligo(ethylene glycol)-terminated silanes on silicon. The influence of various parameters has been examined in order to optimize the treatment in terms of cleanliness, thickness and density (AFM, X-ray reflectometry, XPS) of the obtained layer. Adsorption of different proteins is used to evaluate the inertness of the background and the selective adsorption on the patterns. RGD immobilization is realized by photografting an azide which bears an active ester able to react with the NH@sub 2@ groups of the ligand. The influence of the nanopatterned surfaces on the adhesion and spreading of neural cells will be examined.

2:40pm **NS+BI-TuA3 Enzymatic Nanofabrication: Step-wise Synthesis of DNA Scaffolds on Nanopatterned Oligonucleotide Templates**, ***D. Chow***, *W.-K. Lee, S. Zauscher, A. Chilkoti,* Duke University

Nucleic acid nanopatterns can serve as a template for step-wise synthesis for a variety of complex molecular nanostructures and have significant potential in materials science, molecular electronics, and biosensing. However, most nanofabrication techniques of nucleic acid scaffolds require DNA to be synthesized separately prior to self-assembly or manipulation at the nanoscale. Enzymes that can polymerize DNA are potentially useful molecular tools for the in situ synthesis of DNA scaffolds. Although these proteins are well studied and commercially available, they have not been previously exploited for enzymatic nanofabrication. This study demonstrates that terminal deoxynucleotidyl transferase repetitively adds mononucleotides to the 3' end of oligonucleotides on gold substrate nanopatterned by e-beam lithography. Without complex multi-step chemistry or biochemistry, the step-wise synthesis of DNA scaffolds leads to significant extension of DNA. This strategy can be modified to create more complex DNA nanostructures by simply replacing natural mononucleotides with unnatural ones, which serve as specific recognition sites along the single-stranded DNA. This enzyme-mediated nanofabrication methodology offers a new route to selectively dock nanoscale components of interest along the vertical direction with nanometer-level precision, and also provides a foundation for fabrication of hybrid molecular ensembles of biotic and abiotic components.

3:00pm **NS+BI-TuA4 Surface Modification and Morphological Stabilization of Silver Nanoparticles**, ***V.H. Perez-Luna***, *A. Dalwadi, S. Lee,* Illinois Institute of Technology

Metallic nanoparticles exhibit unique optical properties due to the oscillation of surface plasmons when excited by visible light. These optical properties are shape dependent and different modes of excitation can occur for anisomeric nanoparticles (e.g. due to transversal and longitudinal oscillation of surface plasmons). Thus, the optical properties of these systems can be changed without modifying their chemical composition. A wide variety of methods for the synthesis of anisomeric metallic nanoparticles (e.g.; triangular slabs, multipods, nanorods) have been developed over the last couple of decades. However, technological applications of these systems have not been extensively implemented in spite of their great potential for surface enhanced emission of fluorescence and Raman scattering. One of the biggest obstacles is the inherent morphological instability of these systems and processing difficulties that may lead to irreversible aggregation. Surface modification of gold and silver nanoparticles with alkane thiol based self-assembled monolayers could help circumvent these problems and allow for technological applications with great potential in biodetection assays. Experimental studies will be presented illustrating the improved morphological stability and tailored properties of surface modified nanoparticles. Experimental evidence of the strong influence exerted by metallic surfaces on emission of fluorescence will be presented. The potential of surface modified Ag and Au nanorods will be discussed with particular emphasis on biological detection assays.

3:20pm **NS+BI-TuA5 Functionalization and Electrical Characterization of Vertically Aligned Carbon Nanofibers**, ***K.-Y. Tse***, *S.E. Baker, E.A. Hindin, T.L. Clare, R.J. Hamers,* University of Wisconsin-Madison

Vertically Aligned Carbon Nanofibers (VACNFs) represent a new form of carbon with potential applications ranging from biosensing to energy storage. We have explored the electrical properties of bare and chemically-functionalized VACNFs in electrolyte solutions using electrical impedance spectroscopy and cyclic voltammetry. Electrical measurements show that the capacitance of the nanofiber forests is directly proportional to the average nanofiber length, demonstrating that the entire fiber surface is electrically active. A comparison of nanofiber forests with planar electrodes shows that the forests have approximately 7 times higher effective surface area. Measurements of DNA hybridization with DNA-modified VACNFs show a similar ratio, showing that the nanofibers have good biological accessibility. We will discuss the factors that control the electrical properties of nanofibers in electrolyte solutions, the effects of nanofiber aggregation, and prospects for the application of nanofibers for biosensing.

3:40pm **NS+BI-TuA6 Single Porphyrin Molecules as Information Storage Elements***, **H. Kim**, Y. Kuk,* Center for Science in Nanometer Scale (CSNS), Korea

Redox behaviors of porphyrin molecules have been widely studied for the possible application to molecular-based information storage for two main reasons; i) they form stable radicals whose redox potentials can be tuned by the synthetic design and chelating metal ions. ii) Assembled on the substrate adequately, they exhibit considerably long charge retention times. Recently, it was shown that they can survive silicon device processing,@footnote 1@ which provides a new possibility to molecular electronics. It was, however, confirmed only for a close-packed monolayer of porphyrins to act as information storage. We separated porphyin molecules both from each other and from the substrate by making a mixed self-assembled monolayer of alkanethiol-derivatized porphyrins and alkanethiols on a Au(111) surface. Alkanethiol monolayers can act as an organic insulating layer whose resistance shows approximately exponential dependence on the chain length and the HOMO-LUMO gap is about 9eV. These properties allow us to investigate more intrinsic behaviors of organic molecules attached to alkanethiol monolayers on surface. By means of scanning tunneling microscopy and spectroscopy, we identified the porphyrin groups on the insulating alkanethiol monolayer and resolved the redox states and the charge retention time of a single porphyrin molecule. @FootnoteText@ @footnote 1@ Molecular memories that survive silicon device processing and real-world operation, Z. Liu et al., Science 302, 1543 (2003).

Plasma Science and Technology
Room 302 - Session PS-TuA

Dielectric Etch II

Moderator: C. Cui, Applied Materials

2:00pm **PS-TuA1 A New Wafer Level Micro Arcing Mechanism in 90nm CVD Low-K Via Etch on 300mm SOI Substrate***, **H. Cong**, C. Low, R.P. Yelehanka, X. Zhang, C. Perera, W. Liu, J.B. Tan, L.C. Hsia,* Chartered Semiconductor MFG Ltd, Singapore

As semiconductor industry moves to 300mm platform and 90nm technologies and beyond, wafer level micro arcing (WLMA) becomes more frequent in dielectric etch. In this paper, we describe the finding of a new WLMA mechanism and the process regime optimization to prevent it happening. In SICOH via etch, high polymer chemistry is needed for better selectivity to both photo resist and underneath barrier. But on the other hand, a high ion energy plasma is required to achieve a good process widow. The etching tool we used is a 300mm capacitively coupled plasma (CCP) high-gap reactor, which has 60Mhz and 2Mhz RF power source applied on top and bottom electrode individually. During our initial via etch process development, C@sub4@F@sub6@/CH@sub3@F etc.were used as via main etch chemistry for better PR selectivity and striation performance. However, we occasionally encountered WLMA at wafer edge around guard rings. Bare Si wafer was used to check RF parameters during the etch process. Spikes were occasionally observed on lower Vpp and C@sub2@ position traces at the beginning of over etch step. We found that there was a powdery polymer deposited on the upper electrode after main etch step and the plasma instability is irrelevant to incoming material. This WLMA phenomenon is different from the experience on MERIE or CCP low-gap reactor. Therefore, we propose a new WLMA mechanism. In SIOCH via etch, main etch step chemistry generates heavy non-uniform polymer deposition on upper electrode. When the process switches to over etch step (normally high DC bias), the polymer out gassing from upper electrode will introduce non-uniformity e-field in the plasma and it triggers WLMA. New main etch chemistry was developed and proved successful for production. We also compared RF parameters during via etch on both SOI and bulk Si substrate, there is no significant difference with new developed recipe. Wafer full map electrical and KLA defect scanned results show free of WLMA.

2:20pm **PS-TuA2 CD and Etch Front Control with Reduced Plasma Damage in Etch and Ash Processes for Porous low-k Materials***, **R. McGowan**,* SEMATECH*; B. White,* SEMATECH & AMD

We present requirements and methods for improvement of performance in low-k dielectric integrations using various etch and ash processes in back end of line applications. The correct etch and ash chemistry is the key to minimizing surface modifications. The use of porous ultra low-k materials is required to achieve an ultra low keff stack. These materials present new challenges to etch and ash engineers due to their low mechanical strength, porous nature and propensity to plasma damage. Plasma Etch and strip processes cause modifications to the dielectric that reduce the effectiveness of the low-k material. It will be necessary to pick materials with minimal chemical susceptibility to damage, and to develop new etch, ash and cleans processes that cause less damage. We use two layer metal test vehicles. A 90nm CVD (k=2.5) and a 130nm "late poragen burn-out" low-k (k=2.1). This paper presents a discussion on the stack integrations and the etch/ash approaches for each. Both integrations are VFTL (via first, trench last) with no embedded stop layers. Smooth etch fronts through etch and ash steps are key to the integrity of the metal barrier and to reliability performance. We will show the etch and ash chemistries required for each low-k and methods to control plasma damage to the low-k. Polymer deposition and its removal are controlling factors in damage control in the etch/ash processes. An investigation of effects from ash chemistries and reactors for plasma damage and impact on profiles will be presented. Interactions between processes, and their impact on the resulting profiles, will be given. Hardmask chemistries are particularly damaging & methods to damage reduction in these etches will be shown. Data will be presented on the rates and ash rates for ULK materials and the impact of the same process on plasma damage. It is shown that the ash process can be used to smooth the etch front to provide a smoother etch front.

2:40pm **PS-TuA3 Influence of Plasma Modulation on low-k Etching in High Density Fluorocarbon Plasmas***, **V. Raballand**, G. Cartry, C. Cardinaud,* Nantes University, France

Low dielectric constant materials (low-k) are used as interlevel dielectrics in integrated circuits. Materials studied are porous and non porous methylsilsesquioxane polymers (SiOCH), as well as amorphous hydrogenated silicon carbide (SiCH), used as hard mask and/or etch stop layer. We study the influence of bias, and source power modulation on low-k etching in high density CHF@sub 3@ based plasma. In addition, low-k etching mechanisms are investigated by using plasma diagnostics (OES, Langmuir probes) correlated with surface analysis (XPS). We use a 13.56 MHz Inductively Coupled Plasma source mounted above a diffusion chamber where the substrate is biased separately. Etch rates are measured in real time by in-situ multi-wavelength ellipsometry. First, only the bias voltage is pulsed. By decreasing the duty cycle (dc), the threshold between etching and deposition is shifted toward higher bias voltage. Moreover, this threshold common for all materials in continuous mode (around - 40V), is now equal to - 50V for porous SiOCH and - 80V for SiCH when pulsing at 1kHz with dc=0.45. Selectivities exceed 10 on a large bias window (50V), while they only reach 6 in continuous mode. Then, we simultaneously pulse the source power and the bias power. Low-k etch rates and selectivities are measured for various ON-time and OFF-time periods. We observe that when the ON-time period is smaller than the time for the plasma to be in stable regime, selectivities are enhanced. To complete these studies, some pattern transfers are realized and compared in continuous and pulsed modes (pulsed bias, or pulsed bias and plasma). Finally, surface compositions and plasma characteristics are analysed. Etching mechanisms are determined in pulsed and continuous modes.

3:00pm **PS-TuA4 Control of Surface Reactions during Organic Low-k Dry Etching***, **S. Uchida**, M. Hori,* Nagoya University, Japan*; K. Oshima, A. Ando, K. Nagahata, T. Tatsumi,* Sony Corporation, Japan

In the fabrication of Cu/low-k interconnect for 45-nm devices and beyond, precise control of plasma processes becomes indispensable. Hybrid dual damascene structures use organic low-k and SiOCH films for trench and via levels. The N-H-based plasma has been employed to fabricate SiLK@super TM@ trench patterns with high selectivity both to SiO@sub 2@ hard mask and to underlying SiOCH. First, to separate the effects of ion energy and radical compositions, the etching yield of SiLK@super TM@ was investigated by using a beam experiment apparatus with a radical injection system. An Ar@super +@ ion beam (100â?"500eV) was used to irradiate sample surfaces (SiLK@super TM@, SiOCH, and SiO@sub 2@) with supplying N and H radical fluxes. We quantitatively varied both the incident ion energy and the composition of the H/N radical fluxes. H and N radical densities were measured by in-situ vacuum ultraviolet absorption spectroscopy. The threshold ion energy for the SiLK@super TM@ etching was about 100 eV under the condition of H / (H + N) = 11%. The etch yield of SiLK@super TM@ strongly depended on the composition of the radical fluxes. We found that H radicals promoted reactions of N atoms with organic polymers. Consequently, the etch yield of SiLK@super TM@ dramatically increased when a small amount of H radicals (< 20%) were added to the N radicals. This result suggests that the stably controlling of the H radical density in N/H plasma and the incident ion energy in real etching systems is important. The high energy peak of the ion energy distribution function was controlled by adjusting the power and frequency in a CCP system. By decreasing the high energy peak (to decrease the etch yield of the hard mask) while keeping the ion current and etch yield high (to keep a high etch rate for SiLK@super TM@ to decrease the total etch time), we have successfully minimized the erosion of the hard mask and the variation of the critical dimension during SiLK@super TM@ trench fabrications.

3:20pm **PS-TuA5 Modeling of Organic Low-k Etching in a Two Frequency Capacitively Coupled Plasma in N@sub 2@/H@sub 2@**, ***K. Ishihara***, *C. Shon, T. Yagisawa, T. Shimada, T. Makabe,* Keio University, Japan

The dimension of ULSI device elements continues to shrink in size and multi-layer interconnect system with Low-k materials is employed to reduce RC signal delay in interconnect. We have two main groups of Low-k materials, i.e., organic and inorganic. Low-k materials have distinct characteristics, such as poor mechanical strength and low heat transfer. Under these circumstances, low tempareture plasma source with low damage is practically needed for Low-k material etching. Capacitively coupled N@sub 2@/H@sub 2@ plasma in parallel plate geometry is considered to be the source for organic Low-k material etching. N and H radicals produced in the collision dominated plasma will play important roles on the characteristics of the etching. In our previous work, we have investigated plasma characteristics in N@sub 2@(50%)/H@sub 2@ in two frequency capacitively coupled plasma (2f-CCP) reactor by using VicAddress. In the present study, we have developed the radical transport to the wafer in 2f-CCP by considering the production paths in both gas and surface phases, and obtained the velocity distribution of ions, H@super +@, H@sub 2@@super +@, H@sub 3@@super +@, and N@sub 2@@super +@ incident on the wafer surface. The radical density agrees well with the experimental. Feature profile evolution in a patterned organic Low-k material will be demonstrated in the 2f-CCP reactor in N@sub 2@(50%)/H@sub 2@.

3:40pm **PS-TuA6 Vacuum-Ultraviolet Photon Irradiation Effects in Fluorocarbon Plasmas on SiO@sub 2@ Etching Surface Reactions using In vacuo Electron-Spin-Resonance**, ***K. Ishikawa,*** Tohoku University, Japan*; Y. Yamazaki, S. Yamasaki,* AIST, Japan*; S. Noda, Y. Ishikawa, S. Samuakwa,* Tohoku University, Japan

Using in vacuo electron-spin-resonance (ESR) technique, where the real defect state can be detected without oxidation effect in air,@footnote 1@ surface reactions of fluorocarbon plasma etch of SiO@sub 2@ films were studied. To understand the reaction mechanism on the surface, creation of dangling bonds (DBs) on the surface are indeed a key process. In this study, we investigated the irradiation effects of vacuum ultraviolet (VUV) or ultraviolet (UV) photons on the surface reactions in the plasma etching processes through observation of the DBs creation. Soon after the plasma process, ESR spectra were measured following transferring to the ESR cavity under vacuum ambient. Experimental results showed that DBs are efficiently created by irradiation of plasma emissions such as VUV and UV photons. In fluorocarbon polymer, C-DBs with surrounding F atoms (Hyperfine interaction of 9.1 and 3.4mT.) are created by emissions of CF@sub 4@ plasmas (Intensive radiation in UV range at about 250nm by CF@sub x@). In amorphous fluorocarbon (a-C:F) films, the C-DBs may play roles of enhancement both of adsorption of gaseous CF@sub x@ radicals and of removal itself by bond-breaking in the polymer. On the other hand, Si-DBs (E' center) in the SiO@sub 2@ film are created by irradiation of emissions in VUV range below 140nm (Most of radiation in atomic emissions such as C, F, and Ar). We speculate tentatively that not only reactive species but also plasma characteristics as emissions affect to creation of the DBs, and the created DBs contributes on the surface reactions of the fluorocarbon plasma etching processes, especially employing high density plasmas. @FootnoteText@ @footnote 1@ K. Ishikawa, et al. Appl. Phys. Lett. 81, 1773 (2002).

Surface Science
Room 202 - Session SS1-TuA
Compound Semiconductors

Moderator: A.A. Baski, Virginia Commonwealth University

2:00pm **SS1-TuA1 Doping Semiconductor Nanocrystals**, ***S.C. Erwin***, Naval Research Laboratory*; L. Zu,* U. Minnesota*; M.I. Haftel, A.L. Efros, T.A. Kennedy,* Naval Research Laboratory*; D.J. Norris,* U. Minnesota **INVITED**

Doping---the intentional introduction of impurities into a material---is fundamental to controlling the properties of bulk semiconductors. The prospect of new technologies has motivated similar efforts to dope semiconductor nanocrystals since their discovery two decades ago. Despite some successes, many of these efforts have failed, for reasons that remain mysterious. For example, individual Mn atoms can be incorporated into nanocrystals of CdS and ZnSe, but not into CdSe---despite comparable solubility limits near 50 percent in the bulk crystals. These difficulties have hindered the development of important new materials, including p- and n-type, and even magnetic, nanocrystals. Such failures have often been attributed to "self-purification,'' an allegedly intrinsic mechanism in nanocrystals whereby impurities are expelled to the nearby surface. Here we propose a very different view: that doping is controlled instead by the initial adsorption of impurities on the nanocrystal surface during growth. We show that impurity adsorption---and therefore doping efficiency---is determined by three main factors: the surface morphology of the nanocrystal, its overall shape, and the tendency of surfactants in the growth solution to bind the impurity. Calculated Mn adsorption energies and equilibrium shapes for several cubic and hexagonal nanocrystals lead to specific doping predictions. These are confirmed by measuring how the Mn concentration in ZnSe varies with nanocrystal size and shape. Finally, we use our predictions to incorporate individual Mn impurities into previously undopable CdSe nanocrystals. This success establishes that earlier difficulties with doping are not intrinsic, and suggests that a variety of doped nanocrystals---for applications from solar cells to spintronics---can be anticipated.

2:40pm **SS1-TuA3 Scanning Tunneling Microscopy Study of Square Manganese Tetramers on Mn3N2(001)**, ***R. Yang***, *H.Q. Yang, A.R. Smith,* Ohio University

The growth of transition metal nitride layers has been a subject of significant interest due to their unique electronic, magnetic, and structural properties. We have previously investigated the growth of Mn3N2 on MgO(001) by molecular beam epitaxy (MBE).@footnote 1@ Mn3N2 is a layer-wise antiferromagnet with magnetic moments of ~ 3 mu_B.@footnote 2@ Two orientations ((010) and (001)) of this structure were grown controllably on MgO(001),depending on the growth conditions. As the bulk structure corresponds to 2 layers of MnN followed by 1 layer of Mn in a fct arrangement, scanning tunneling microscopy (STM) shows that the (010) surface consists of row structures.@footnote 3@ These rows correspond to the Mn planes, which are perpendicular to the surface. Here we present results for the (001) surface in which the Mn planes are in the surface plane. However, this presents an interesting question regarding the epitaxial Mn3N2 (001) growth surface, due to the MnN-MnN-Mn stacking sequence of the atomic layers in bulk. If the stacking sequence extends to the surface, then different structures should be observed on adjacent terraces. Again, these films are grown on MgO(001) substrates by MBE. STM images show smooth terraces and atomic steps. On certain of the terraces a unique and new reconstruction is seen, resolved as square Mn tetramers in a c(4x2) structural arrangement. Two domains of the tetramer reconstruction, rotated by 90 deg to each other, occur. A model is presented for this square Mn tetramer reconstruction, in which the Mn atoms of the tetramer layer belong to the Mn layer at the surface in the MnN-MnN-Mn stacking sequence. @FootnoteText@ @footnote 1@Yang et al., J. Appl. Phys. 91(3), 1053 (2002). @footnote 2@G. Kreiner, and H. Jacobs, J. Alloys and Comp. 183, 345 (1992). @footnote 3@Yang et al., Appl. Phys. Lett. 78, 3860 (2001). .

3:00pm **SS1-TuA4 Investigations of Surface Reconstructions and 3D Roughening in InGaAs Films**, ***L.E. Sears***, *J.M. Millunchick,* University of Michigan*; C. Pearson,* University of Michigan - Flint

The epitaxial growth of III-V semiconductors and their corresponding properties depend on the surface reconstructions and morphology of the film grown. We have found that the surface structure of In@sub x@Ga@sub 1-x@As alloys consists of multiple surface reconstructions depending on the composition x. The goal of this work is to determine which reconstructions are present as a function of both composition and temperature, in order to map out the surface phase diagram for this system. For example, for In@sub 0.81@Ga@sub 0.19@As/InP grown at 503°C with an As overpressure of 2.1 ML/sec and a growth rate of 1.16 ML/sec, highly ordered regions of @beta@2(2x4) coexist with more disordered regions having a (4x3) symmetry. In this case, the percentage of @beta@2(2x4) covering the surface initially increases with increasing thickness, followed by a sharp decrease that corresponds to the onset of surface roughening and 3D roughening. Previous work on In@sub 0.27@Ga@sub 0.73@As/GaAs, which has a similar lattice mismatch, shows similar disordered (4x3) regions, but the highly ordered @beta@2(2x4) regions have been replaced by @alpha@2(2x4) regions.@footnote 1@ It is postulated that the (4x3) surface reconstruction is a unique alloy structure, while the (2x4) reconstructions are enriched in In. @FootnoteText@ @footnote 1@ Millunchick JM, Riposan A, Dall B, Pearson C, and Orr BG, Surf. Sci. 550 (1-3): 1-7 FEB 10 2004.

3:20pm **SS1-TuA5 SiO/GaAs Charge Build Up Induced Pinning*, D.L. Winn,* *M.J. Hale,* University of California, San Diego

The correlation between atomic bonding sites and the electronic structure of SiO on GaAs(001)-c(2x8)/(2x4), was investigated using scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and density functional theory (DFT). At low coverage, STM images reveal that SiO molecules bond Si-end down; this is consistent with Si being under-coordinated and O being fully-coordinated in SiO. At ~5% monolayer (ML) coverage, multiple bonding geometries were observed. To confirm the site assignments from STM images, DFT calculations were used to estimate the exotherimicties of the different bonding geometries. However, the sites predicted to be most stable were not the most abundant sites observed in the STM experiments. To rectify the discrepancy between calculations and experiments, a total energy vs. SiO chemical potential plot (i.e. SiO coverage) was constructed. Once the bonding geometries were deduced, STS measurements were preformed, which showed that SiO pins the Fermi level at ~5% ML coverage. Density of state (DOS) and partial density of state (PDOS) calculations revealed that only certain bonding geometries pin the Fermi level.

3:40pm **SS1-TuA6 Phosphine and Tertiarybutylphosphine Adsorption on the Indium-Rich InP (001)-(2x4) Surface*, R.L. Woo,*** *S.F. Cheng, G. Chen, Y. Sun, R.F. Hicks,* University of California, Los Angeles

Phosphine (PH3) and tertiarybutylphosphine (TBP) are widely used as the group V sources during the MOCVD growth of P-containing compound semiconductors and their alloys. The kinetics of PH3 and TBP adsorption and phosphorus desorption from InP (001) have been studied using optical techniques and reflectance difference spectroscopy. It is found that the sticking probability of TBP decreases from 0.007 to 0.001 with increasing temperature from 420 to 520 ËsC; whereas the sticking probability of PH3 is approximately equal to 0.001 over the same range. In this report, we present a vibrational study of TBP and PH3 adsorption on the indium-rich InP (001)-(2x4) surface. Both molecules form a dative bond to exposed indium atoms on the surface. A fraction of these species decompose to PH2 or PH species with hydrogen and tertiarybutyl ligands transfering to nearby phosphorus sites. The initial datively bonded state explains the low sticking probability of these molecules, as reversible desorption competes effectively with irreversible dissociative adsorption at elevated temperatures.

Surface Science

Room 203 - Session SS2-TuA

Tribology, Adhesion and Friction

Moderator: K.J. Wahl, Naval Research Laboratory

2:00pm **SS2-TuA1 Temperature Dependence of Nanoscale Friction*, A. Schirmeisen,*** *L. Jansen, H. Fuchs,* University of Muenster, Germany

Friction processes at the nanoscale are the focus of numerous research projects, yet a comprehensive picture is still lacking. Despite the fact that most of the proposed models for energy dissipation in point contacts inherently depend on the sample temperature, this issue has been rarely addressed in experimental work. In this contribution we present nanoscale friction experiments with an ultrahigh vacuum atomic force microscope (AFM), where the sample temperature was varied by two orders of magnitude from 30 K to 300 K. Two different materials have been investigated: Graphite and silicon. On HOPG graphite atomic scale "stick-slip" is typically observed. Tribological properties of silicon contacts are of great interest in the area of MEMS/NEMS technology, where friction and wear are an important issue for the technical application of these devices. On graphite the overall friction increases monotonically when lowering the sample temperature. This behaviour can be understood in the framework of atomic scale "stick-slip" friction. The temperature influences the probability of the tip to jump between adjacent potential minima, in effect causing friction to decrease with increasing temperature.@footnote 1@ In contrast, the friction temperature curves on silicon show a rather complex behaviour, with a pronounced friction maximum at 100 K. Similar peaks have been found before in experiments, where internal friction properties of macroscopic vibrating silicon membranes were measured@footnote 2@ Those so-called "Debye-peaks" are related to thermally activated creation of defects in the bulk material, which leads to a strong enhancement of energy dissipation at the Debye temperature. We will discuss some of the intriguing similarities between our nanoscopic friction measurements and the concept of the Debye-peaks in bulk material. @FootnoteText@ @footnote 1@ Sang et al., Phys. Rev. Lett. 87 (2001) 174301@footnote 2@ Berry and Pritchet, J. Appl. Phys. 67 (1990) 3661.

2:20pm **SS2-TuA2 Capillary Adhesion and Tribology involving Adventitious Water on SiOx Surfaces*, J.E. Houston,*** Sandia National Laboratories

Thin water films adsorbed on surfaces are very important in interfacial interactions and can be critical in determining the behavior and stability of MEMS and NEMS-type devices, which are dominated by extremely high surface to volume ratios. In this presentation, the results of a study are discussed concerning the interfacial interaction of a silica tip and an O-H terminated SiOx surface as a function of both temperature and relative humidity. The study utilizes Interfacial Force Microscopy (IFM) and involves measurements of the normal and frictional forces as a function of interfacial separation. The results indicate, even at very low humidities, that the force profiles are characteristic of a capillary interaction. In addition, the behavior of the lateral force shows significant levels of friction upon capillary formation, increasing further as the two surfaces approach. Upon separating the surfaces, a small hysteretic behavior is observed but with little indication of the "snap-out" instability normally associated with meniscus rupture. These measurements are repeated as a function of tip speed, relative humidity and temperature in order to gain insight concerning the thickness of the water layers, their viscosities and the rates of capillary condensation and evaporation. These results are contrasted with those from similar experiments involving self-assembled monolayer films terminated by combinations of -CH3 and -COOH end-groups. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

2:40pm **SS2-TuA3 Aqueous Based Lubrication: Fundamental Studies of Polymer Brushes Adsorbed at Oxide Surfaces*, S.S. Perry,*** *X. Yan,* University of Houston*; N. Spencer, S. Lee, M. Mueller,* Swiss Federal Institute of Technology, Switzerland **INVITED**

The development of synthetic polymer lubricants to mimic joint lubrication within the human body will be presented. Unlike most industrial applications involving oils and greases, lubrication of these joints is accomplished in an aqueous environment. Fundamentally, water is a poor lubricant in most settings due to the weak pressure dependence of its viscosity, yet the contacting surfaces of skeletal joints function with low friction throughout a lifetime. Motivated by the molecular structure of materials making up joint surfaces, interfacial friction between polymer brush surfaces under aqueous environments has been probed with an array of molecularly sensitive surface analytical techniques including atomic force microscopy. The brush surfaces, comprised of poly(L-lysine)-g-poly(ethylene glycol) (PLL-g-PEG), have been generated through the spontaneous adsorption of polymer from solution onto oxide substrates and sodium borosilicate surfaces (AFM tip). The character of the polymer films has been investigated in-situ with the quartz crystal microbalance (QCM) and atomic force microscope (AFM) and ex-situ with ellipsometry and X-ray photoelectron spectroscopy (XPS). The interfacial friction measurements have been carried out on polymer-coated substrates with bare or polymer-coated, microsphere-attached tips in over a range of solution conditions. It was found that the adsorption of polymer on oxides strikingly reduced the interfacial friction, resulting in ultra-low friction under certain conditions. By using a series of PLL-g-PEG polymers differing from each other in PEG side-chain length and grafting ratio, we observed that frictional properties of polymer-coated interfaces strongly depend on the architecture of PLL-g-PEG. Polymer-film formation and the influence of polymer architecture will be reviewed while the role of solvent and manifestation of ultra-low friction will be discussed in detail.

3:20pm **SS2-TuA5 Molecular Dynamics Simulations of the Nanotribological Behavior of a Polytetrafluoroethylene Transfer Films*, I. Jang*,** *W.G. Sawyer, S.R. Phillpot, S.B. Sinnott,* University of Florida

Mechanical devices for space applications need to be able to operate reliably in an extreme range of environments. Therefore, the physical and chemical integrity of the materials has to be assured under extremes of both high and low temperature, under ambient pressures and in near absolute vacuum, and under solar radiation. Polytetrafluoroethylene (PTFE) is known to have good thermal and chemical stability, and a low frictional coefficient. Thus polymer nanocomposites based on PTFE are considered to be promising materials for solid lubricant in aerospace applications. Like other polymer materials, many properties of PTFE depend on morphology. By changing the polymeric chain structure and combining it with other materials, it is likely that the frictional coefficient of PTFE can be made lower and its wear resistance further improved. In order to develop new material systems with superior frictional properties or to improve the existing ones, it is necessary to understand the detailed mechanisms of their frictional behavior, and the effect of molecular structure on friction. In this study, molecular dynamics (MD) simulations are performed to examine the effect of chain configuration on the frictional behavior of PTFE at the molecular level, with the aim of identifying the fundamental wear mechanisms, and guiding the further refinement of the materials with low frictional coefficients for space applications.

3:40pm **SS2-TuA6 Correlation of Frictional and Thermal Properties with Molecular Chain Order in Self-Assembled Monolayers of Organosilanes on Silicon*, S. Sambasivan,*** National Institute of Standards and Technology*; S. Hsieh,* National Institute of Standrads and Technology*; D.A. Fischer, S. Hsu,* National Institute of Standards and Technology

n-Alkyltricholorosilanes films with different chain lengths (Cn films where n=5-30) were characterized by Near edge x-ray absorption fine structure (NEXAFS), FTIR and AFM. The information afforded from these complementary techniques has provided the unique opportunity to interpret the frictional properties of the monolayer films in relation to the molecular assembly and chain lengths. In this study, we use the non-destructive x-ray absorption technique NEXAFS to quantitatively measure the surface (~6nm) molecular orientation of SAMs (self-assembled monolayers). We observe that the chain lengths having 12, 16 and 18 carbon atoms are highly oriented with a preferential molecular orientation of the polymeric C-C chains perpendicular to the surface. C5 and C30 SAMs did not exhibit preferential orientation of the alkyl chain and C10 showed partial ordering. Complimentary FTIR studies were done to estimate order qualitatively by peak positions of asymmetric CH@sub 2@ and the symmetric CH@sub 2@ stretches. The molecular order information from FTIR followed similar trends as determined by NEXAFS. The frictional properties of the organic monolayers were determined through the simultaneous measurement of normal (load) and lateral (friction) interfacial forces with AFM. Friction measurements on different chain lengths follows similar trends with surface order calculated from NEXAFS. In-situ heating and NEXAFS experiments on C16 films reveal that C16 film were well ordered up to 200°C and heating beyond that temperature it transitions from partially ordered to completely disordered/destroyed at 350°C. AFM images show a significant change in surface morphology after annealing. Friction force measurements indicated an increase after heating to 350°C, values approaching close to the friction forces from bare Si wafer. Our results show that the degree of ordering in the SAM governs the friction properties of the film.

Surface Science
Room 206 - Session SS3-TuA
Ultrafast Surface Dynamics

Moderator: I. Harrison, University of Virginia

2:00pm **SS3-TuA1 Probing Molecular Motion Induced by Femtosecond Laser Pulses on a Site-by-Site Basis with Scanning Tunneling Microscopy,** *L. Bartels,* University of California, Riverside*; F. Wang, D. Moeller,* Columbia University*; E. Knoesel,* Rowan University*; **T.F. Heinz,*** Columbia University **INVITED**

The fundamental time scale for nuclear motion and energy flow in surface dynamics lies in the femto- to picosecond range. With the on-going advances in laser technology, many powerful new approaches have been developed to explore the dynamics of elementary surface processes directly in the time domain. In this paper, we present an application of femtosecond laser radiation to examine the dynamics of the elementary process of surface diffusion. To this end, femtosecond laser irradiation is used to excite adsorbed CO molecules on a Cu(110) surface; the ensuing motion of individual molecules across the surface is characterized on a site-to-site basis by in-situ scanning tunneling microscopy (STM). Adsorbate motion both along and perpendicular to the rows of the Cu(110) surface occurs readily, in marked contrast to the behavior seen for equilibrium diffusion processes. In addition, STM permits us to determine the rate of the concurrent laser-induced desorption process. The experimental findings for the efficiency and direction of the molecular motion can be understood as a manifestation of strong coupling of the lateral degrees of freedom of the adsorbed molecules to the substrate electronic excitation produced by the femtosecond laser radiation. The overall efficiency for surface diffusion is modeled using data on the thermal diffusion of CO/Cu(110) in conjunction with a description of coupling of the frustrated translational mode to the electronic and lattice excitation of the substrate. The dominant role of the substrate electronic excitation emerges from this analysis. The experiment represents a successful combination of the capabilities of utlrafast laser radiation for accessing non-equilibrium phenomena and the capabilities of STM for accessing the atomic length scale. Possible future research directions will be discussed.

2:40pm **SS3-TuA3 Ultrafast Laser Modification of Single Crystal MgO Surfaces@footnote 1@*, J.T. Dickinson,*** *S.C. Langford,* Washington State University*; W.P. Hess,* Pacific Northwest National Laboratory*; L.A. Boatner,* Oak Ridge National Laboratory

Interactions between wide bandgap insulators and nanosecond pulses of laser light at sub bandgap wavelengths often require defects for both absorption and emission. With ultrafast pulses, multiphoton absorption across the bandgap is much more probable and often yields exciton mediated decomposition. The doubly charged lattice of materials like MgO strongly inhibits exciton-induced decomposition. We compare the response of (100) MgO to 100 fs pulses at wavelengths of 800, 400, and 267 nm with our earlier studies using nanosecond pulses at 248 nm and 193 nm, where the latter interactions were clearly defect-mediated. Surfaces modified by femtosecond pulses show evidence for both photothermal and photoelectronic processes when examined by AFM and SEM. Some of these processes are clearly mediated by defects. @FootnoteText@ @footnote 1@This work was supported by the Department of Energy.

3:00pm **SS3-TuA4 Wavelength-Dependent Infrared Laser Induced Hydrogen Desorption from a Si(111) Surface*, Z. Liu,*** University of Minnesota, Vanderbilt University*; P.I. Cohen,* University of Minnesota*; L.C. Feldman, N.H. Tolk,* Vanderbilt University*; Z. Zhang,* Oak Ridge National Laboratory

Wavelength-dependent infrared laser induced hydrogen desorption from a Si(111) surface hydrogen passivation on silicon surfaces is a bottleneck in low temperature Si homoepitaxy. We employ infrared laser radiation from the Vanderbilt Free-Electron Laser to desorb hydrogen from a Si(111) surface at a temperature below 300C where thermal effects are minimal. The vibrational mode of the Si-H bond was excited by the infrared laser to enhance hydrogen desorption. The cross-section of the coupling between the laser and the Si-H bonds has been measured as a function of laser wavelength and power, showing a resonant effect at the energy of the vibrational mode at 2087 cm@super -1@. The desorption rate was maximized when the polarization of the light was maximized along the Si-H bond direction. The vibrational energies of the Si-H bond are different at terrace sites and step sites. Thus this mechanism provides a way to selectively desorb hydrogen atoms from different locations on the Si surface, and allows site-selective epitaxial growth of Si. To our knowledge this it the first report of wavelength-selective desorption of an adsorbate on a semiconductor surface. This project is partially supported by DARPA/SPAWAR grant N66001-04-1-8924 and DOE grant ER45781.

3:20pm **SS3-TuA5 Surface Plasmon Oscillation in Gold Nanocrystals of Different Shapes: Some Radiative and Nonradiative Ultrafast Properties*, M. El-Sayed,*** Georgia Institute of Technology **INVITED**

The surface plasmon oscillation in gold nanocrystals will be introduced and its enhancement of the absorption, fluorescence and scattering properties will be discussed as a function of shapes. Excited with femtosecond lasers, the electronic oscillation rapidly relaxes into phonon excitation. The lattice oscillation can be detected optically as it modulates the surface plasmon absorption (the color) of the nanocrystals. The dependence of this oscillation on size, shape and interparticle coupling will be discussed

Thin Films
Room 306 - Session TF-TuA

Atomic Layer Deposition - Metals
Moderator: S. Rossnagel, IBM

2:00pm **TF-TuA1 Materials Available by ALD**, ***R.G. Gordon,*** Harvard University **INVITED**

Atomic later deposition (ALD) can deposit pure thin films with precisely-controlled, uniform thickness and composition over large areas and on aggressive topologies. ALD is a vapor deposition process based on sequential self terminating surface reactions where the precursor vapors are injected separately in pulses added to a flowing carrier gas, separated by a purge of excess precursor vapor. Each pulse and purge sequence constitutes an ALD half-cycle. Ideally, each half-cycle adds a uniform new layer of material and then the reaction stops even if more precursor vapor arrives at the surface. This self-terminating character results in ALD's uniformity, conformality and precise thickness control. To achieve ALD's unique characteristics, ALD precursors must have very specific properties: high reactivity with surfaces (but not with themselves), high thermal stability, along with adequate volatility. In addition, their reaction byproducts must not react with the deposited films. Precursors with metal-nitrogen bonds have been found to be particularly effective for ALD of metal oxides, nitrides, silicates, phosphates and pure metals: dialkylamides of Al, Sn, Ti, Zr, Hf, Nb and Ta; dialkylamide-alkylimide mixed ligand compounds of Nb, Ta, Mo and W; dialkylacetamidinates of Mg, Ca, Sc, Ti, V, Cr, Mn, Fe, Ru, Co, Ni, Cu, Bi, Y, La and the other lanthanide metals. Examples of the materials made from these precursors include high-k dielectric insulators HfO@sub 2@, HfON, HfSiON and LaAlO@sub 3@; electrical conductors of Cu; conducting Cu diffusion barriers of WN and TaN@sub x@; metals Co and Ru that promote strong adhesion between Cu and nitride diffusion barriers; magnetic metals Fe, Co and Ni and their magnetoresistive combinations with Al@sub 2@O@sub 3@ or MgO; photonic crystals of high-dielectric constant material Ta@sub 3@N@sub 5@; insulating AlN for passivating Ge surfaces; conformal silica layers for insulation in microelectronics, and for optical interference filters and nano-optical devices.

2:40pm **TF-TuA3 Ru ALD and Applications for Advanced Devices**, ***H. Lee,*** *S.J. Lim, W.J. Maeng, H. Kim,* POSTECH, South Korea

Ru has good properties such as low resistivity, high thermal stability, and nobility. Thus, the atomic layer deposition (ALD) of Ru has been required for many applications in nanoscale device fabrication including memory capacitor electrode, Cu electroplating seed layer, and CMOS gate electrode with the scaling of devices. Although ALD of Ru has been reported by several groups previously, there are still crucial problems to be solved including the poor nucleation and practical limitation caused by the use of oxidant as a reactant. To address these problems, we have performed comparative studies using different Ru precursors including cyclopentadiel, pentadienyl, and carbonyl based precursors on various practically important substrates including Si, SiO@sub 2@, Ta@sub 2@O@sub 5@, TaN, and TiN. Also, plasma enhanced ALD using hydrogen and nitrogen plasma has been performed. Very low resistivity (as low as 10µ@ohm@cm) Ru with excellent conformality was obtained and the in situ plasma treatment produced promising results to enhance nucleation behavior. The microstructure of Ru layer as well as interface between Ru and substrates and chemical and electrical properties have been characterized. The results will be discussed focusing on the future semiconductor device applications including electrode and Cu electroplating seed layer.

3:00pm **TF-TuA4 Atomic Layer Deposition of Ruthenium on Organic Self Assembled Monolayers for Work Function Tuning**, ***K.J. Park,*** *D.B. Terry, G.N. Parsons,* North Carolina State University

Ruthenium is of interest for advanced metal/oxide/ semiconductor (MOS) transistor gate electrodes to reduce poly-silicon depletion and as a nucleation layer for copper interconnects. Patterned self assembled monolayers have previously been used to impede nucleation during ALD processing. In this work, metal atomic layer deposition was achieved on self-assembled monolayers, where the tail groups were chosen to promote, rather than impede nucleation, and the effect of the monolayer on the work function of the metal in an MOS capacitor is characterized. Specifically, Ru was deposited using bis-(cyclopetandienyl) ruthenium and oxygen onto HfSiO@sub x@, SiO@sub 2@, and onto 3-aminopropyltriethoxysilane (APTES) and undecenyl tricholosilane (UDS) monolayers formed on HfSiO@sub x@. Self-limiting atomic layer deposition was achieved at temperatures between ~310° and 350°C, corresponding to ~1 Å per deposition cycle. Capacitance vs. voltage (CV) with various thicknesses of dielectric was measured at 1MHz using p-type silicon substrates with doping levels of 1.5x10@super 18@ cm@super -3@, to determine the effective workfunction (@PHI@@sub m,eff@) of the ALD metal. The organic monolayer undergoes some reaction and modification during the metal ALD step, however CV measurements show relatively stable behavior at room temperature, with large changes observed after a 400°C forming gas anneal, suggesting stability of the monolayer during deposition. Ru on untreated HfSiO@sub x@ gives @PHI@@sub m,eff@ = 4.7 eV, whereas the APTES treated surface shows an increase in @PHI@@sub m,eff@ to about 4.8 eV, and a decrease to about 4.2 eV for the UDS surface. The shifts are consistent with dipoles in the monolayers at the organic/dielectric interface. The ability to deposit metal by ALD onto organic surfaces will likely be useful for a variety of advanced organic device structures.

3:20pm **TF-TuA5 Quartz Crystal Microbalance Measurements of W ALD Nucleation on Al@sub 2@O@sub 3@**, ***R.A. Wind,*** *F.H. Fabreguette, S.M. George,* University of Colorado

Nucleation phenomena can critically affect the growth of nanolaminates using atomic layer deposition (ALD). A good example is W/Al@sub 2@O@sub 3@ nanolaminates where the nucleation of W ALD on Al@sub 2@O@sub 3@ limits the minimum thickness of a continuous and ultrasmooth W nanolayer to ~25 Å. Quartz crystal microbalance (QCM) studies can measure the mass gain per cycle (MGPC) during ALD with a precision of ~0.4 ng/cm@super 2@. QCM investigations of W ALD nucleation on Al@sub 2@O@sub 3@ reveal complex behavior. During optimum nucleation conditions, WF@sub 6@ exposures lead to mass gain but Si@sub 2@H@sub 6@ exposures produce no measurable mass gain for the first 2 cycles. After 3 cycles, the MGPC for both reactants increases and reaches a maximum after 8 cycles for WF@sub 6@ and after 12 cycles for Si@sub 2@H@sub 6@. The total MGPC exhibits a "ringing" behavior and a second maximum is observed before reaching the steady state growth rate. For different reactant exposures, the positions of the first and second maxima in the MGPC shift to a longer number of cycles. Modeling of these QCM results is in agreement with three-dimensional W island growth that produces a maximum in the MGPC. This maximum corresponds to the largest W surface area prior to the coalescence of the W islands. The existence of these W islands is confirmed by atomic force microscope (AFM) measurements. The changing ratio of the WF@sub 6@ and Si@sub 2@H@sub 6@ MGPCs is consistent with distinct growth regimes. These different ratios suggest that the relative density of reactive surface sites evolves as W islands are created, grow, and coalesce prior to forming a continuous W film.

3:40pm **TF-TuA6 Novel ALD Reactor Design and Metrology Study for Tungsten ALD Process**, ***W. Lei,*** *L. Henn-Lecordier, G.W. Rubloff,* University of Maryland

We have developed a novel wafer-scale atomic layer deposition (ALD) reactor which incorporates small reaction volume for short cycle time, multi-mode operation for process flexibility, and in-situ chemical sensing for rapid process learning and control. A movable cap within the UHV chamber enables transfer and enclosure of the wafer within a 0.2 L mini-reactor. Operation is possible using steady-state flow with alternating gas species or using fill-and-pumpout cycling of each gas with pumpout acceleration by lifting the cap to employ the larger reactor volume as ballast. Downstream in-situ mass spectrometry (MS) provides direct process sensing. By integrating reaction product MS signal over each exposure, we are able to observe nucleation and linear film growth stages of ALD film growth and study nucleation kinetics under different process and initial surface conditions, which indicated the application of in-situ MS for advanced process control in ALD process. First wafer effects in in-situ MS sensing are apparent when a sequence of wafers are processed, particularly when time delays are introduced between wafers; this is attributed to concurrent reaction on mini-reactor walls, where different gas exposure history is encountered. Advanced process control can be improved by proper pre-process reactor treatment to reduce first wafer effect.

Vacuum Technology
Room 200 - Session VT-TuA

Calibration: Pressure and Flow Metrology

Moderator: P.J. Abbott, NIST

2:00pm **VT-TuA1 A New Determination of the Volume Ratio of the NPLI Static Expansion System*, P. Mohan,*** National Physical Laboratory, India

Recently we have acquired high accuracy resonant silicon gauges of two different ranges, one 130 kPa full scale and the other 1 kPa full scale, for measurement of the initial and final pressures. These gauges have been utilized in a cumulative expansion process for the measurement of the volume ratio of the NPLI Static Expansion System which is nominally 2820. With these new gauges, and with the use of calibrated Platinum Resistance Thermometers mounted inside the vacuum chambers, it has been possible to measure the volume ratio with a relative expanded uncertainty (k=2) of 0.0015. The standard thus characterized has been used to calibrate SRGs at a number of pressures in the range 0.1 Pa to 1 Pa in steps of 0.1 Pa. The Gauge Constant at each of these pressures, defined as equal to the ratio of the indicated pressure to the true pressure is then plotted against the true pressure. The resulting straight line plot has a negative slope and its intercept equals the gauge coefficient. The two SRGs, NPL-0 and NPL-2 thus calibrated are used (i) as a device for measuring the pressure rise in the flowmeter of the NPLI orifice flow system and (ii) as a secondary standard for the calibration of the user gauges.

2:20pm **VT-TuA2 Precise Volume Measurement of Bellows with its Length for a Constant Pressure Flowmeter*, K. Arai,*** *H. Akimichi, M. Hirata,* AIST, Japan

A constant pressure flowmeter has been used to generate very low gas flow from 10@super -5@ to 10@super -10@ Pa m@super 3@ s@super -1@ as a reference standard to calibrate standard leaks. The rate of the flow is obtained by a volume change in a time while the pressure is kept constant. There are several methods to change the volume of the flowmeter. Bellows directly elongated and shortened by a pulse-driven linear actuator was used for precise measurements of the displacement and low outgassing due to the all-metal structure. In this study, the volume change in the bellows was measured as a function of its length by Boyle's law. The flowmeter was isolated from pumps and gas sources. The ratio of the volume change to the initial volume was obtained from the ratio of the pressures before and after shortening the bellows. The absolute value of the volume change was obtained from the difference of the pressure ratio by introducing a well-known volume (ball bearings). Pressure measurements were performed by capacitance diaphragm gauges (CDGs). The repeatability of the pressure ratio measurements was 3x10@super -5@, which was comparable to the chamber temperature fluctuation of 30 mK. The deformation of the bellows was caused by a pressure difference between inside and outside of the bellows. The pressure difference was kept under 2500 Pa by controlling the outside pressure. The remaining deformation was compensated by the value of the pressure difference. The volume change in the bellows by shorting it by 25.00 mm was 32.24 ml. The uncertainty of the measurement was 0.07% after consideration of the temperature fluctuation, the difference from the ideal gas and the thermal transpiration effect of the gauge. The volume changed with its length quadratically, as estimated from the structure of bellows.

2:40pm **VT-TuA3 High-accuracy Vacuum Calibration System*, S. Tison,*** *S. Lu, S. Sukumaran,* Mykrolis Corporation

Many industrial vacuum processes require high-accuracy vacuum measurements to enable process capabilities critical to the device attributes or performance. Semiconductor device manufacture, flat panel displays, optical coatings, and vacuum metalurgy are a few examples where vacuum measurements are critical to product performance. While these measurements are critical, there is a lack of high accuracy industrial calibration systems that can support these needs; particularly at pressures below 100 Pa. A new vacuum calibration system has been developed for calibrating vacuum gages in the range of 1 Pa to 100 kPa with uncertainties ranging from +/-0.02% to +/-0.2% of reading. The paper describes this system which utilizes high stabilty transfer standards in conjunction with pressure expansion techniques to achieve reliable high-accuracy vacuum gage calibration and characterization. The data indicates that automated high accuracy vacuum measurements can be made with a single vacuum system utilizing transfer standards in conjunction with a "primary type" pressure expansion technique which relies on the known ratio of two calibrated volumes to achieve accuracies previously unachievable solely by utilizing vacuum transfer standards.

3:00pm **VT-TuA4 Development of a New High-Stability Transfer Standard Based on Resonant Silicon Gauges for the Range 0.1 kPa - 130 kPa*, J.H. Hendricks,*** *A.P. Miiller,* NIST

The National Institute of Standards and Technology (NIST) has developed a new transfer standard capable of absolute-mode and differential-mode operation in the range 0.1 kPa to 130 kPa. The transfer standard is based on Resonant Silicon Gauges (RSGs) of the same type used to provide superior calibration stability in recent CCM Key Comparisons of absolute and differential pressure standards,@footnote1,2@ which covered pressures up to 1 kPa. The new NIST transfer standard consists of two 10-kPa RSGs, two 130-kPa RSGs, and an ion pump to provide a reference vacuum when making absolute pressure measurements. The pairs of RSGs provide redundancy but, more importantly, they enable Youden analyses to be applied to the data to identify systematic differences between pressure standards. The RSG transfer standard package has demonstrated good short term zero stability and pressure resolution over the 0.1 kPa to 130 kPa range, and has demonstrated long term instability of a few ppm at 130 kPa, increasing to 0.01% at 0.1 kPa. In terms of long term stability, the new NIST transfer standard package is nominally commensurate with piston gauges at pressures down to 10 kPa, and extends measurement capability down to 0.1 kPa. Although its intended use is for intra-laboratory comparisons of primary standards at NIST, this transfer standard may also find applications in international comparisons of pressure standards. @FootnoteText@ @footnote 1@ Miiller, A. P., Bergoglio, M., Bignell, N., Fen, K. M. K., Hong, S. S., Jousten, K., Mohan, P., Redgrave, F. J., and Sardi, M., Final report on key comparison CCM.P-K4 of absolute pressure standards from 1 Pa to 1000 Pa, Metrologia, 2002, 39, Tech. Suppl., 07001.@footnote 2@Miiller, A. P., Cignolo, G., Fitzgerald, M. P., and Perkin, M. P., Final report on key comparison CCM.P-K5 of differential pressure standards from 1 Pa to 1000 Pa, Metrologia, 2002, 39, Tech. Suppl., 07002.

3:20pm **VT-TuA5 New Calibration Apparatus for 1, 10, 100 Torr Capacitance Diaphragm Gauges*, S.Y. Woo,*** *I.M. Choi,* Korea Research Institute of Standards and Science, Korea

Capacitance diaphragm gauges are electromechanical pressure sensors in which the displacement of a stretched thin metal diaphragm is detected by a capacitance measurement. They have gained widespread international popularity not only as high accuracy transfer standards but also as reliable replacements for many other vacuum gauges used in process industries. In order to calibrate such accurate vacuum gauges, laser or ultrasonic mercury manometers have been used. However, complexity, health concerns of mercury vapor, and cost of these manometers made it difficult to use in most calibration laboratories. As a substitute, a gas-operated pressure balance can be used with some modifications. In this article, we introduce a new apparatus for the calibration of the precise vacuum gauges. This device has a unique mass handling structure that allows masses to be changed in-situ without breaking the vacuum. It covers three pressure ranges of 1 Torr, 10 Torr, and 100 Torr. Using this apparatus, the characteristics of three commercial vacuum gauges (MKS, Model 626) were studied.

3:40pm **VT-TuA6 Real Time Calibration of Leak Detection Sensitivity*, X. Chen,*** *T.B. Huang, L.B. Xiao, L.Z. Cha,* Tsinghua University, China

The most important characteristic for leak detection is the smallest leak rate that an instrument, method, or system is capable of detecting under specified conditions. It is used to call the smallest detectable leak rate the leak detection sensitivity. One permeation type reference leak with a fixed leak rate is commonly used to calibrate the leak detector and the method has been standardized. It is no doubt that is basic and important to guarantee the instrument in optimized condition. However, the real level of the leak detection sensitivity depends on not only the test instrument, but also the system and methods. The detection limit will be higher or lower if the partial flow pump or accumulation method is used. Sensitivity calibration is necessary to distinguish between leak detector and leak detection. The demand for quantitative leak tests has increased sharply in recent times because the information is more important for the quality control. Real time calibration of the leak detection sensitivity can be achieved by comparing the tested leak rate with a fixed reference leak rate, a series of such reference leak rates or a variable reference leak rate. The last one is optimal for calibration since it provides the reference leak rate in the similar range of the tested leakage rate under the real situation. An adjustable reference leak rate system is put forward with wide dynamic range from 10 @super -7@ to 10 @super -14@Pa.m @super 3@ /s by changing the inlet helium pressure and concentration of a platinum wire-glass reference leak with molecular flow characteristics. The real time calibration for the leak detection has been realized quantitatively not only for the instrument, including the ultra sensitive MSLD system, but also for the methods and system, even for the ultra sensitive leak detection. The detected leak rate under the real situation can be quantitatively calibrated which attracts more and more attention but has not been standardized until now.

Electronic Materials and Processing
Room Exhibit Hall C&D - Session EM-TuP

Electronic Materials and Processing Poster Session

EM-TuP1 Nano-scale Characterization of High-k Dielectric Materials by Conducting Atomic Force Microscopy*, S. Kremmer, H. Wurmbauer,* ***C. Teichert,*** University of Leoben, Austria*; G. Tallarida, S. Spiga, C. Wiemer, M. Fanciulli,* Laboratorio MDM - INFM, Italy

The steadily shrinking device dimensions in semiconductor industries demand for advanced electrical characterization methods operating on the nanometer scale. One suitable technique already used for the evaluation of silicon gate oxide quality@footnote 1,2@ is Conducting Atomic-Force Microscopy (C-AFM). C-AFM, operating in ultra high vacuum (UHV), is used to study different high-k dielectric thin films with regard to their electric properties and homogeneity. The UHV conditions are mandatory here to avoid surface modification during the experiment. ZrO@sub 2@ and HfO@sub 2@ films of different thickness have been grown by atomic layer chemical vapor deposition on silicon substrates. With increasing film thickness their structure changes from amorphous to polycrystalline with different phases. Therefore, local current-voltage measurements are used to obtain a statistical distribution of the leakage current as a function of applied voltage and film thickness. Further, two dimensional current scans are performed to obtain the local distribution of leakage current. These investigations provide a deeper insight into the influence of crystallites formation on nano-scale electrical properties of two selected dielectric materials. @FootnoteText@@footnote 1@ S. Kremmer, C. Teichert, E. Pischler, H. Gold, F. Kuchar, M. Schatzmayr, Surf. and Interf. Anal. 33 (2002), 168. @footnote 2@ S. Kremmer, H. Wurmbauer, C. Teichert, G. Tallarida, S. Spiga, C. Wiemer, M. Fanciulli, J. Appl. Phys. 97/7 (2005), 74315-1-7.

EM-TuP2 Production of a Hafnium Silicate Dielectric Layer For Use As a Gate Oxide by Solid-State Reaction*,* ***H.T. Johnson-Steigelman,*** *S.S. Parihar, A.V. Brinck, P.F. Lyman,* University of Wisconsin-Milwaukee

The formation of hafnium silicate films (HfSi@sub x@O@sub y@) for use as gate oxides with large dielectric constant by solid state reaction of Hf metal and high quality thermal oxide and native oxide SiO@sub 2@/Si(001) substrates was investigated using LEED, XPS, and AFM. Thin, fully reacted silicate films could be formed, and were thermally stable in vacuum to temperatures in excess of 800°C. Spectroscopic evidence indicates that the interface between a hafnium silicate layer and the silicon substrate was stable against SiO@sub 2@ formation. The observed binding energy (BE) shift provides evidence that the hafnium silicate/Si interface will be stable against interfacial SiO@sub 2@ formation (as predicted by Hubbard and Schlom@footnote 1@). The thermodynamic driving force for interfacial SiO@sub 2@ formation when most oxides are placed in contact with Si is the large heat of formation of the SiO@sub 2@ phase. While Si is rather electro-positive, Hf is even more electropositive, and HfO@sub 2@ has a higher heat of formation than does SiO@sub 2@. The shift of the Si oxide XPS feature to shallower BE indicates@footnote 2@ that Hf donates charge to the SiO@sub 2@ complexes in the newly formed silicate compound. This shift, therefore, corroborates that Hf is able to reduce SiO@sub 2@; conversely, Si will be unable to reduce HfO@sub 2@, and interfacial SiO@sub 2@ formation will be thermodynamically unfavorable. The morphology of the surface was determined by AFM to be smooth and featureless on the length scale of hundreds of nanometers. LEED results show the surface to be amorphous and free of pinholes. @FootnoteText@ @footnote 1@ K.J. Hubbard, D.G. Schlom: J. Mater. Res. 11, 2757 (1996).@footnote 2@ T.L. Barr: Crit. Rev. Anal. Chem. 22, 115 (1991).

EM-TuP3 Investigation of Annealing Effect and Suppression of Hydration and Silicate Formation of La@sub 2@O@sub 3@ Thin Films*,* ***D. Eom,*** *S.Y. No, C.S. Hwang, H.J. Kim,* Seoul National University, Korea

High dielectric constant materials (high-K) have attracted a great deal of interest because of the dramatic scaling down of Metal-Oxide-Semiconductor field effect transistor (MOSFET) device reaching its physical limit in terms of reduction of thickness. Among high-k materials, such as Al@sub 2@O@sub 3@, HfO@sub 2@, HfSiO@sub 4@, ZrO@sub 2@, La@sub 2@O@sub 3@ etc., have attracted a great deal of interest as a replacement for the conventional SiO@sub 2@ gate oxide. La@sub 2@O@sub 3@ is promising as a gate dielectric film in future CMOS devices because it has a large conduction band offset(~2.0eV), high didelectric constant(24~27) and good leakage current characteristic. However La@sub 2@O@sub 3@ films appears to be hydrated easily and become silicate films by react with Si substrate. Moreover improvement of thermal stability is needed like other high-k films. In this work AlN thiln films was deposited after La@sub 2@O@sub 3@ film deposition on Si substrate to suppress hydration of La@sub 2@O@sub 3@ films. From X-ray Photoelectron Spectroscopy(XPS) results the hydration was not shown. AlN thin film was also deposited on Si substrate before La@sub 2@O@sub 3@ film deposition as a barrier material to prevent reaction of La2O3 film with Si substrate. Without thermal annealing, AlN barrier film is effective to reduce silicate formation, but after 800@super o@C annealing the AlN film mixed with La@sub 2@O@sub 3@ film therefore barrier effect disappeared. And There were flat band shift toward negative voltage and degradation of electrical properties after annealing at 800@super o@C and over. From Auger Electron Spectroscopy and XPS results, it is considered to be because of a generation of oxygen vacancy during annealing. Low temperature annealing at O@sub 2@ ambient after 800@super o@C annealing recovered flat band voltage and electrical characteristics.

EM-TuP4 Nucleation Behavior of Ru Thin Films Prepared by MOCVD on TiN Substrate with TiCl@sub 4@ Pre-Treatment*,* ***B.S. Kim,*** *H.S. Seo, C.S. Hwang,* Seoul National University, Korea*; S.Y. Kang, J.Y. Kim, K.H. Lee, H.J. Lim, C.Y. Yoo, S.T. Kim,* Samsung Electronics Co., Ltd., Korea*; H.J. Kim,* Seoul National University, Korea

Due to the excellent characteristics, such as low electrical resistivity and good dry etching property, ruthenium (Ru) is considered as a candidate material for capacitor electrodes in gigabit scale dynamic random access memories (DRAMs). In a typical concave type storage node of gigabit scale DRAMs, the Ru bottom electrodes should be deposited on the TiN diffusion barrier. But the metalorganic chemical vapor deposition (MOCVD) of Ru on the TiN surface has been suffered from the poor nucleation behavior and rough surface morphologies, which makes the capacitor fabrication difficult. In this study, the Ru films were deposited by MOCVD using Ruthenium-(2,4-Demethylpentadienyl)(Ethylcyclopentadienyl)[Ru(DER)] on various substrates, such as Ta@sub 2@O@sub 5@, TiN, SiO@sub 2@ and TiO@sub 2@. The nucleation rate of Ru on the TiN surface was improved by the TiCl@sub 4@ pre-treatment which was done by atomic layer deposition (ALD). The Ru thin films deposited on Ta@sub 2@O@sub 5@ and TiO@sub 2@ with oxygen addition at 300°C have continuous and smooth surfaces while those on SiO@sub 2@ and TiN have discontinuous film morphologies. It is suggested that the different surface morphologies of Ru films were mainly attributed to the difference of bonding type of the substrates. The surfaces with highly ionic bonding characteristics, such as Ta@sub 2@O@sub 5@ and TiO@sub 2@, can share the surface electron cloud with the metallic Ru dimer resulting in lowering of nucleation barrier energy. Therefore surface modification of TiN surface that has highly covalent bonding characteristics can improve the nucleation rate of Ru. The pre-treatment with ALD-TiCl@sub 4@ enhanced the nucleation rate of Ru films mainly due to the partial oxidation of TiCl@sub 4@ that results in the formation of seed-like TiO@sub 2@ layer. The conformal deposition of Ru on the contact-hole structure and on the bottom TiN surfaces was successfully obtained via surface modification using TiCl@sub 4@.

EM-TuP5 Structural and Electrical Properties of PZT Thin Films Patterned by Chemical Mechanical Polishing Process for FRAM Applications*,* ***N.-H. Kim,*** *P.-J. Ko, G.-W. Choi,* Chosun University, Korea*; Y.-J. Seo,* Daebul University, Korea*; W.-S. Lee,* Chosun University, Korea

Ferroelectric random access memory (FRAM) has been considered as one of future memory devices due to its ideal memory properties such as non-volatility, high charge storage, and faster switching for the readywrite operations. The lead zirconate titanate (PZT) is one of the most attractive perovskite-type materials for realizing the ferroelectric products due to its higher remanant polarization and the ability to withstand higher coercive fields. The sol-gel solution of Pb@sub 1.1@(Zr@sub 0.52@Ti@sub 0.48@)O@sub 3@ was spin-coated on patterned substrate. The thin films were polished by chemical mechanical polishing (CMP) technique. The vertical sidewall of the PZT pattern was successfully achieved, because the patterning of the PZT thin films was performed by using a damascene process. In this study, the surface morphology and the electrical properties of PZT capacitors were evaluated after CMP process. The selectivities for end-point detection to top electrode materials and TEOS film were also studied. Surface morphology after CMP process was undergone with atomic force microscopy (AFM) of PSIA Company. The electrical properties were measured between the top and bottom electrodes. Capacitance and leakage current of PZT capacitors after CMP are examined. The capacitance was measured by using an HP 4192 impedance/gain-phase analyzer at 10 kHz, and the leakage current density was determined by using an HP 4145B semiconductor parameter analyzer. The crystal structure of the polished samples was investigated by X-ray diffraction (XRD) to observe the variation of phases. The improved PZT capacitor with the high capacitance and the low leakage current could be obtained by analyzing correlation between electrical properties and various CMP process parameters. Acknowledgement: This work was supported by a Korea Research Foundation grant (KRF-2004-005-D00007).

EM-TuP6 Chemical Mechanical Polishing Characteristics of BTO Thin Films by BaTiO@sub 3@ Abrasive Slurry for High-Density DRAM Application*, **P.-J. Ko**, N.-H. Kim, J. Park,* Chosun University, Korea*; Y.-J. Seo,* Daebul University, Korea*; W.-S. Lee,* Chosun University, Korea

BaTiO@sub 3@ (BTO) high dielectric thin films have received much attention as one of the new dielectric materials for high density dynamic random access memories (DRAMs) because of their high relative dielectric constant and small variation in dielectric properties with frequency. It is well known that BTO films are difficult to be etched by wet etching, but high etch rate with good selectivity to pattern mask was required. Plasma etching provided the high etch rate with good selectivity, however, the problem of sidewall angle still remained to be solved. In this study, we examined the characteristics of submicron capacitors fabricated by chemical mechanical polishing (CMP) process with the vertical sidewall instead of plasma etching. The sputtered BTO thin films on the stopper layer were polished by CMP with commercial alumina (Al@sub 2@O@sub 3@) slurry and self-developed BTO (BaTiO@sub 3@) abrasive slurry. The polishing results of BTO thin films using the harder alumina slurry represented the high removal rate, while the polishing results using the softer BTO slurry shows the relatively low removal rate with insufficient within-wafer non-uniformity (WIWNU%). The polishing mechanism of BTO thin films by two kinds of slurry was investigated by the surface analysis by X-ray photoelectron spectroscopy (XPS) with the surface morphology by atomic force microscopy (AFM). The surface roughness and planarity were also strongly depended on the self-developed BTO slurry. The vertical sidewall of BTO patterns was successfully accomplished by the damascene process of BTO thin film. Acknowledgement: This work was supported by a Korea Research Foundation grant (KRF-2004-005-D00007).

EM-TuP7 Poly(3-hexylthiophene) Organic Thin Film Transistor on Polyimide using Electroplated Au Electrodes*, **J.G. Lee**, Y.G. Seol,* Sungkyunkwan University, South Korea*; N.-E. Lee,* Sungkyunkwan University, South Korea, Korea

Organic thin film transistors (OTFT) on flexible substrate utilizing electroplated Au electrodes have potential advantages in the fabrication of flexible devices requiring large area coverage, structural flexibility, low-temperature processing, and especially low cost. In particular, the application of electroplated electrode with the adhesion layer enables one to obtain reliable devices on the flexible substrate in terms of mechanical flexibility and thermal stability, as proved in the flexible printed circuit board (FPCB) technology. In this work, poly(3-hexylthiophene) (P3HT) OTFT devices with a top-gate structure were fabricated by utilizing the electroplated Au source and drain electrodes on polyimide substrate. First, since the adhesion of electrodes on the flexible substrate is of great importance for the application in flexible devices, the adhesion improvement of electroplated electrode structures was achieved by plasma treatment of polyimide substrate followed by a sequential sputter-deposition of Cr(adhesion) and metal seed layers. Au source/drain electrodes were electroplated into the patterned SU-8 mask by ultra-violet photolithography. After SU-8 ashing and Cr/Cu layer removal, spin-coating of P3HT layers, and gate dielectric formation, and Al electrode deposition were carried out. Here, organic-inorganic hybrid gate dielectric layers as well as organic PVP gate dielectric were employed. The channel length ranged between 5 and 110 µm, and the channel width was 800 µm. Electrical properties of fabricated OTFTs were characterized and the effect of various process conditions and structures on the performances of the fabricated devices will be discussed.

EM-TuP8 Scanning Tunneling Microscopy Study of Rubrene on Au(100) Substrate*, **Y.S. Cho**, Y.J. Song, H.J. Yang, S.H. Kim, Y. Kuk,* CSNS, Seoul National University, Korea

Rubrene has become a strong candidate for an organic thin film transistor (OTFT) because of its high mobility 8 cm@super 2@/Vs,@footnote 1@ and easy processing on various substrates, together with pentacene. It has been pointed out that interface states work as scattering centers and results in poorly reproduced potential barriers for various metal contacts in the transport measurement. In this work, we investigated the geometrical and electronic structures of a single rubrene molecule and up to 10-monolayer rubrene adsorbed on Au(100) surface with scanning tunneling microscopy and spectroscopy. In the geometry of metal-rubrene-metal transport measurement, the molecule is positioned as if it flat on the contact metal. This geometry can be achieved by adsorbing the molecule on a metal substrate. At low coverages, rubrene molecules grow as a single phase from step edges, showing step flow growth. They show well ordered growth pattern at high coverages. We will show the coverage dependence of the HOMO-LUMO gap states and possible implication to the transport measurement. @FootnoteText@ @footnote 1@Vikram C. Sundar et al., Science, 303, 1644 (2004).

EM-TuP9 Organic Light Emitting Diodes Using Alkaline-earth Metals as an Electron-injecting Layer and Their Semi-passivation*, **C.H. Jeong**, J.T. Lim, J.H. Lee, J.H. Lim, G.Y. Yeom,* Sungkyunkwan University, Korea

To obtain the high performance characteristics of the top-emitting organic light-emitting diodes (TEOLEDs) based on an electron-injecting layer of alkaline-earth metal with a low work function, devices consisted of glass/ITO/2-TNATA (60 nm)/NPB (15 nm)/Alq@sub3@ (45 nm)/alkali metal (x nm)/Al (2 nm)/Ag (10-y nm)/Au (y nm)/Alq@sub3@ (53 nm) were fabricated, where, alkaline-earth metals such as Ba, Ca, and Mg were used to reduce the energy barrier from the cathode into the organic layers by electron hopping. The top Alq@sub3@ layer was used to passivate the semitransparent conducting protecting layer (STCPL) composed of alkaline-earth metal/Al/Ag/Au and organic layers from the damaging environment. In addition, the Ag layer composed of STCPL was introduced into TEOLED to improve the adhesion between the Al layer and the Au layer. In this study, the electrical characteristics of the fabricated TEOLEDs semi-passivated with the Alq@sub3@ were measured using an electrometer and the luminescence characteristics were determined by measuring the photocurrent induced by light emission from the OLEDs using a picoammeter. Other properties such as optical transmittance and resistivity were measured using a UV-spectrometer and a four point probe, respectively.

EM-TuP10 Highly-efficient Top-emission Organic Light-emitting Diodes Using Alkali Metal as an Electron-injecting Layer and Their Semi-passivation*, **J.T. Lim**, C.H. Jeong, J.H. Lee, J.H. Lim, G.Y. Yeom,* Sungkyunkwan University, Korea

To obtain high-performance top-emission organic light-emitting diodes (TEOLEDs) with a high aperture ratio and high resolution, a device consisted of glass/ITO/2-TNATA (60 nm)/NPB (15 nm)/Alq@sub3@ (45 nm)/alkali metal (x nm)/Al (2 nm)/Ag (10-y nm)/Au (y nm)/Alq@sub3@ (53 nm) was fabricated. Especially, in this study, alkali metals such as Li and Cs with a low work function was used to reduce the energy barrier from the cathode into the organic layers by electron hopping and the top Alq@sub3@ layer was used to passivate the semitransparent conducting protecting layer (STCPL) composed of alkali metal/Al/Ag/Au and organic layers from the hostile environment. The Ag layer composing of STCPL was introduced into TEOLED to improve the adhesion between the Al layer and the Au layer. In this study, the characteristics of STCPL composed of TEOLEDs were investigated using a four-point probe and a UV-spectroscopy to measure the resistivity and the transmittance, respectively. Also, the current-voltage-luminance characteristics and electroluminescent spectra of the TEOLEDs semi-passivated with the Alq@sub3@ layer were investigated.

EM-TuP11 Oxygen Doping of DNA Molecules Using Rapid Thermal Processor at Low Temperature*, **M.W. Yoon**, J.M. Lee, K.-S. Kim,* Sungkyunkwan University, Korea*; Y.-H. Roh,* Sungkyunkwan University, Korea, Republic of Korea

Recent studies on the electrical conduction of the deoxyribonucleic acid (DNA) strands reveal that they may act as semiconductor materials, suggesting that they might be used for the nano-electronic devices in the future. Furthermore, semiconducting properties can be controlled by gas (e.g., O@sub 2@) doping the DNA molecules. For example, it has been reported that O@sub 2@ doping of poly(dG)-poly(dC) DNA molecules at room temperature results in p-type semiconductor-like DNA molecules. In this work, we investigated the possibility of carrier doping of various types of DNA molecules including poly(dG)-poly(dC), DNA poly(dA)-poly(dT) and lambda DNA molecules at low temperature (e.g., room temperature, 90, 100, 130 °C) using a rapid thermal processor. Doping gases used in this work were N@sub 2@ and O@sub 2@. Annealing at low temperature in vacuum (i.e., without gas doping) was also performed to clarify the roles of both gas sources and heat treatment. Results obtained in this work show that both O@sub 2@ doping and heat treatment have certain roles to change the conduction properties of DNA molecules. Specifically, the conductivity of poly(dG)-poly(dC) molecules increases as annealing temperature raises regardless of the gas types. However, the highest value of conductivity at given annealing temperature was always obtained from the samples annealed at O@sub 2@ ambient, suggesting that O@sub 2@ doping is more effective to make p-type semiconductor-like poly(dG)-poly(dC) molecules. On the contrary, O@sub 2@ doping of poly(dA)-poly(dT) and lambda DNA molecules results in the reduction of conductivity. This phenomenon suggests that poly(dA)-poly(dT) and lambda DNA molecules behave like a n-type semiconductor due to O@sub 2@ doping.

EM-TuP12 Field Effect Properties of M-DNA Molecules Observed by Changing Gate Voltages*, J.M. Lee,* Sungkyunkwan University, Korea*; Y.-H. Roh,* Sungkyunkwan University, Korea, Republic of Korea

Recent studies on the electrical conduction of the deoxyribonucleic acid (DNA) strands reveal that they may act as semiconductor materials, suggesting that they might be used for the nano-electronic devices in the future. Consequently, on-going research efforts have been focused on ways to find the conduction properties of many different types of DNA strands. In addition, several research groups reported that the metallic nano-wires can be formed by utilizing the DNA molecules as templates. One of the examples is the formation of M-DNA (i.e., metallic DNA). M-DNA is a complex form of DNA molecules with the divalent metallic ions (i.e., Zn@super 2+@) replacing the imino proton of every base pair. Because of containing metallic ions at DNA helix, it has been reported that the current-voltage characteristic of M-DNA attached on the two-terminal electrode represents the metallic properties, although I-V data failed to show the ohmic property. In this work, we investigated the I-V characteristics of M-DNA molecules attached on the three-terminal electrode. We monitored the current variation measured between source and drain by sweeping the gate voltage. It has been reported that M-DNA can be made using poly(dA)-poly(dT), poly(dG)-poly(dC) or lambda DNA. For the current work, we report the experimental results obtained from M-DNA prepared using lambda DNA. Once M-DNA molecules were trapped on the top electrode, the sample chamber was evacuated to minimize the humidity effects on the measurement of I-V characteristics. We found that the current of M-DNA molecules measured between source and drain (I@sub DS@) increases as the gate voltage increases, although the degree of current modulation obtained through M-DNA was less than that of lambda DNA. Since the I@sub DS@ data obtained in this work were collected in vacuum, we suggest that the I@sub DS@ modulation caused by the gate voltage is due to the field effect.

EM-TuP13 Simple Patterning Techniques for Fabrication of Organic Thin Film Transistors*, S.J. Jo,* *W.J. Kim, C.S. Kim, H.K. Baik,* Yonsei University, Korea

Fabrication of any device requires patterning and this patterning for organic devices such as OTFTs presents a challenge because of the deleterious effects a solvent typically used in conventional lithography can cause. Particularly in the context of low cost, large volume manufacturing, there is a need to demonstrate that inexpensive material deposition and patterning processes can be integrated with existing device concepts with adequate performance. As an alternative to the vacuum deposition and photolithographic patterning of the various functional films, the use of high-resolution patterning techniques is of particular interest. We report simple microcontact printing techniques to form organic source/drain microstructure for organic thin film transistors (OTFTs). Fabrication of OTFTs with micron feature sizes demonstrates the approach. The performance of these transistors compares with that of similar devices constructed using conventional methods and Au source/drain.

EM-TuP14 Encapsulation of Pentacene Thin-Film Transistors with a Transparent Oxide/Organic Smoothing Layer*, W.J. Kim,* *W.H. Koo, S.J. Jo, C.S. Kim, H.K. Baik,* Yonsei University, Korea

The long-term stability of the pentacene thin-film transistors encapsulated with a transparent oxide which was prepared by ion-beam assisted deposition (IBAD) was investigated in terms of the electrical properties associated with material characterizations. A polymer layer had been deposited in vacuum prior to IBAD process not only for a buffer layer, but also for a smoothing layer. Our unique multi-layer encapsulation was found to effectively suppress water and oxygen permeation into the organic active layer so that our pentacene TFT with the encapsulation showed a greatly enhanced long-term stability. It is thus concluded that our encapsulation can be employed for stable operation of organic devices such as organic thin-film transistors (OTFTs) and organic light-emitting diodes (OLEDs) in air ambient.

EM-TuP15 Photo- and Electro-Luminescence Studies of Highly Alkyl-Substituted Templated Bis(8-Hydroxyquinoline) Derivatives for Organic Light Emitting Diodes*, R.D. Torres,* *P.H. Holloway, J.R. Reynolds,* University of Florida*; M. Albrecht,* RWTH Aachen, Germany

Aluminum tris(8-hydroxyquinoline) (Alq@sub 3@) is the most widely used electon transport and emissive material in organic light emitting diodes (OLEDs). Alq@sub 3@ is thermally and morphologically stable when vacuum deposited. The molecule is shaped to avoid exciplex formation, serves as a good green (@lambda@@sub max@ = 520 nm) emitter with excellent electron-transport properties, and the bandgap can be modified by attaching electron withdrawing/donating organic groups. In this study we have used solution and thin-film photoluminescence (PL) to characterize the emissive properties of new Alq@sub 3@ type derivatives: tetra-decyl-substituted ethylene-linked bis(8-hydroxyquinoline) (BHQ) ligands. The effects of different templating cations (K@super +@, NH@sub 4@@super +@, Rb@super +@, Cs@super +@) on optical emission from these complexes [(ligand)@sub 3@Al@sub 2@ and (ligand)@sub 3@Ga@sub 2@] were investigated. Solutions were prepared using only the complexes, or using the complexes with various molar concentrations of poly(methyl methacrylate) or polystyrene. The ratio of PMMA or PS was varied relative to the polymer repeat unit, and compared to similarly prepared Alq@sub 3@ solutions. Thin films were made by spin coating on glass substrates. The samples were excited with a 350 nm excitation, and spectra were recorded from 400 to 650 nm. Electroluminescent devices with structures of glass/ITO/PEDOT-PSS HTL/BHQ complexes ETL/LiF/Al were prepared. The current-voltage-luminescence characteristics of these devices were observed. These complexes show promise as Alq@sub 3@ derivatives that can be processed by methods other than vacuum evaporation.

EM-TuP16 A Study of the Optical and Electronic Properties of Poly(Vinylidene Fluoride-Trifluoroethylene) Copolymer Thin Films*, Y.X. Li,* Shandong University, China*; L. Yan, E.A. Irene,* University of North Carolina-Chapel Hill

Thin films of poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] have been deposited by spin casting onto bare Si and SiO@sub 2@ coated on Si substrates. From trials with a variety of solvents methyl ethyl ketone (MEK) yielded the most uniform smooth films as determined using atomic force microscopy. The films were found to be optically transparent in the 280-830 nm (1.5-4.5eV) optical range. Spectroscopic ellipsometry (SE) was used to obtain the refractive index in the 1.5-4.5eV photon energy range that was found to decrease with thinner films. SE performed at several sensitive angles of incidence has revealed no measurable optical anisotropy. Annealing in vacuum caused about a 3% decrease in thickness and an increase of about 0.02 in the refractive index. Capacitance versus voltage (C-V) and conductance (G(@omega@)) versus gate voltage (G(@omega@)-V) measurements were performed on capacitor structures in order to determine K, interface charge and the density of interface states (D@sub it@), respectively. Thus far a value of about 9 was obtained for the static dielectric constant for 50nm films and interface charge and D@sub it@ results appear promising for the use of P(VDF-TrFE) as a gate dielectric and thin film piezoelectric for various electronic applications. @FootnoteText@ This research is supported by NASA URETI and the NSF.

EM-TuP17 Optical and Interfacial Electronic Properties of Spin Cast Poly(o-methoxyaniline) (POMA)Thin Films*, R.P. Shrestha,* *D.X. Yang, E.A. Irene,* University of North Carolina-Chapel Hill

Optical properties of semiconducting polymer, Poly(o-methoxyaniline)(POMA) thin films prepared by spin casting have been studied and using optical transmission spectroscopy and spectroscopic ellipsometry in the visible-near uv optical range. The dispersion in refractive index and extinction coefficient along with anisotropy, surface roughness and annealing results are reported.@footnote 1@ Small uniaxial anisotropy has been measured and annealing leads to some densification and surface smoothing. Capacitance versus voltage (C-V)and current versus voltage (I-V) measurements were performed on capacitor and thin film transistor (TFT) structures, respectively. The C-V results indicate to yield a value of about 5 for the static dielectric constant. The I-V yields TFT transfer characteristics are used to optimize the film formation process and the performance of thin film POMA as a P-type semiconductor for TFT's. @FootnoteText@ @footnote 1@R.P. Shrestha, D. Yang, and E.A. Irene, Ellipsometric determination of the Optical Properties of Poly(o-methoxyaniline), Thin Solid Films, submitted Feb 2005.

EM-TuP20 Contact Properties in Metal/Molecule/GaAs Devices*, **P.D. Carpenter**, S. Lodha, Q. Hang, D.B. Janes,* Purdue University

Molecular devices have typically been fabricated in a metal/molecule/metal configuration.@footnote 1@ However, the use of semiconductor contacts in molecular devices allows for control in device performance by varying the doping density and the surface properties of the semiconductor substrates. Semiconductors, such as GaAs, also allow for stable bonds to molecular layers. In this work, molecular devices have been fabricated in a metal/molecule/GaAs device structure using standard photolithography techniques and solution-based growth of self-assembled monolayers (SAMs).@footnote 2@ After SAMs were formed on the GaAs surface, a top metal contact was formed using an indirect path, low energy evaporation technique. The effect of the doping density (n-type and p-type) and surface properties of the substrates, including surface layers incorporating defect states, have been studied in devices employing both aromatic and alkanethiol SAMs. An electrostatic model was developed to calculate the energy band diagrams of the structures and to explain the current-voltage results. Upon examination of the I-V characteristics of the devices, we see an increase in conductivity from the fabricated metal/semiconductor control devices. It has been shown that the electrical performance of the device can be modulated by changing the coupling of the molecular monolayer with the top contact metal and the GaAs substrate. This coupling can be changed by varying the work-function of the metal contact, or by changing the doping type in the GaAs or by incorporating defect states near the GaAs surface.@footnote 3@ Alternate metallization techniques, including shadow masking approaches to avoid process-related damage to the SAM, have also been developed. @FootnoteText@ @footnote 1@ M. Reed, et. al., Science, vol. 278, pp. 252-254 (1997).@footnote 2@ S. Lodha and D. B. Janes, et al., Appl. Phys. Lett., vol. 85, 2809 (2004).@footnote 3@ S. Lodha, P. D. Carpenter, and D. B. Janes, unpublished.

EM-TuP22 Effect of Fluorine-Neutral Beam Irradiation on the Ohmic Contact Formation to n-type GaN*, **H.C. Lee**, J.W. Bae, B.J. Park, G.Y. Yeom,* Sungkyunkwan University, Korea

Irradiation of a fuorine-neutral beam to n-type GaN surface is expected to create nitrogen vacancy at the near surface region of the GaN due to the removal of nitrogen by forming NFx(x=1-3) volatile gases, which may act as donor impurities. In the case of n-type GaN contact formation, it is well known that the increase in the donor concentration at the surface region of the GaN is one of important factors to achieve a good ohmic formation. The increase of carrier concentration should lead to a decrease of the effective barrier height between n-GaN and contact material, implicating a decrease of the depletion region width. Consequently, more carriers can tunnel through the reduced barrier, resulting in ohmic contact behavior. To date, few investigators have been using chlorine-based plasmas to generate N-vacancies at the surface region of the GaN. However, these charged and energetic treatments may lead to an electrical damage to the GaN layer, which can be attributed to the deterioration of contact property. On the other hand, a treatment by a neutral beam may give no electrical damage to the GaN layer due to its neutrality. It is noteworthy that the creation of N vacancy without electrical damage causes an increase in the net carrier concentration in the near surface region of n-GaN, resulting in the decrease of the contact resistivity. Therefore, in this study, a fluorine-neutral beam is proposed to remove nitrogen atoms off at the surface of n-type GaN without electrical damage. The subsequent ITO-based contact schemes including ITO, Ti/ITO, and Cr/ITO have been investigated using a current-voltage measurement system, photoluminescence (PL) and X-ray photoelectron spectroscopy (XPS). In this presentation, the advantage of fluorine-neutral beam treatment to modify n-GaN surface, as compared to a reactive ion treatment will also be discussed.

EM-TuP23 Effect of Nitrogen Contents (0%-5.3%) on the Temperature Dependence of Photoluminescence in InGaAsN/GaAs Single Quantum Wells*, **F.-I. Lai**,* National Chiao-Tung Univ., Taiwan*; S.-Y. Kuo,* National Applied Research Labs, Taiwan*; J.S. Wang,* Opto-Electronics & Systems Labs of the Industrial Technology Research Institute, Taiwan*; H.C. Kuo,* National Chiao-Tung Univ., Taiwan*; J.Y. Chi,* Opto-Electronics & Systems Labs of the Industrial Technology Research Institute, Taiwain*; S.C. Wang,* National Chiao-Tung Univ., Taiwan*; H.S. Wang, C.T. Liang, Y.F. Chen,* National Taiwan Univ.

A series of InGaAsN/GaAs single-quantum wells (SQWs) with N contents varied from 0 % to 5.3 % were grown by molecular-beam epitaxy using a solid As and nitro-gen plasma sources. The impact of nitrogen concentration on the optical properties, as determined by the temperature dependence of photoluminescence (PL), of a 6 nm SQW was investigated. In the low-temperature region, a pronounced temperature-dependent S-shaped peak positions was observed in PL spectra while increasing nitrogen concen-tration. Two approaches are used to estimate the localization energy and a strong cor-relation was observed. Quenching behavior reveals that the defect-related nonradiative processes might enhance in the highly nitrogen incorporated samples and thus influence the recombination dynamics. In addition, the evolution of the peak positions of In-GaAsN/GaAs samples was in agreement with the empirical Varshni model in the high-temperature region. A significant reduction in the temperature dependence of the emission peak position compared to the nitrogen-free InGaAs SQW is analyzed as well, and further confirms the prediction of proposed band anticrossing model of the elec-tronic structure of III-N-V alloys.

EM-TuP25 Preparation of Indium Nitride Thin Films by RF-MOMBE*, **S.-Y. Kuo**, C.-C. Kei,* National Applied Research Laboratories, Taiwan*; C.K. Chao,* National Central University, Taiwan*; C.Y. Su, C.N. Hsiao,* National Applied Research Laboratories, Taiwan

Indium nitride (InN) films have been prepared directly on the c-plane sapphire substrate by a self-designed radio-frequency plasma metal organic molecular beam epitaxy (RF-MOMBE) system. We have investigated the influence of growth temperature on the surface morphology and crystal structures by x-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). At growth temperatures higher than 500 @super o@C, the hexagonal wurtzite InN films exhibit randomly oriented crystalline nature. Furthermore, a pronounced two-dimensional growth mode was observed at the growth temperature of 500 @super o@C, and this film shows highly orientation along the c-plane. These results indicate that the control of growth temperature is essential for engineering the growth of InN on Al@sub 2@O@sub 3@ (0001), and it might be also applicable for other lattice-mismatched III-V heteroepitaxial systems.

EM-TuP26 Electron Spin Resonance Investigation of the Crystallization of Silicon Carbide Thin Films*, **M. Tabbal**, E. Hannoun, T. Christidis, S. Isber,* American University of Beirut, Lebanon

Crystalline silicon carbide (SiC) is the material of choice to manufacture electronic devices that can function under extreme conditions such as high temperature, high power, high frequency and high radiation environments. This work consists of an electron spin resonance (ESR) study of paramagnetic defects in crystallized SiC thin films. The films were synthesized on silicon (Si) substrates by ablating a pure SiC target in vacuum using a pulsed KrF excimer laser. Crystallization of the films was performed by deposition at temperatures exceeding 1000 K and by subsequent high temperature annealing. ESR measurements were performed at various temperatures at X-Band and Q-Band frequencies. It is found that deposition at temperatures between 1000 and 1200 K lead to polycrystalline films with an ESR signal having a g-value of 2.0028, that is attributed to carbon defects. Increasing the deposition temperature lead to a decrease in the spin density as well as broadening of the ESR signal, with typical line-widths ranging between 5.5 and 8 G. In addition, the ESR line was found to be temperature dependent with lines narrowing down to 4.8 G for measurements performed at 77 K. Such broadening phenomena could be explained by an enhanced connectivity of the paramagnetic defects that could lead to conducting channels in the layers. Post-deposition annealing of the films, in vacuum, to 1400 K leads to a considerable decrease in spin density as well as to significant narrowing of the ESR signal down to 3.2 G. Furthermore, annealing was found to eliminate the temperature dependent contribution to the ESR line-width. These effects were found to occur along with an enhancement of the crystalline quality of the films, as deduced by XRD. A phenomenological model describing the effect of deposition temperature and subsequent annealing on the paramagnetic defects in polycrystalline SiC films will be presented.

EM-TuP27 Remote Plasma-Enhanced Chemical Vapor Deposition of Tantalum Diffusion Barrier*, E.R. Fisher, **P.R. McCurdy**,* Colorado State University

In recent years, copper (Cu) has become the interconnection material of choice, replacing aluminum (Al) and Al alloys in integrated circuits (ICâ?Ts). Cu is preferred over Al because of its lower resistivity and higher melting point. The lower resitivity is especially important in reducing the resistance-capacitance delay, which becomes dominant as the gate size continues to decrease. Unfortunately, Cu is susceptible to diffusion into SiO2, and suffers from poor adhesion to low dielectric constant materials. Therefore, it is imperative to have a diffusion barrier that can also act as an adhesion layer to integrate Cu into ICâ?Ts. Currently, tantalum (Ta) and Ta nitrides are widely used for this purpose. Ta metal is especially attractive because of its low resistivity; however, because of the ever increasing aspect ratio of metal lines, tradition methods for depositing Ta metal are deficient. Physical vapor deposition is a line-of-sight method that does not work well on high aspect ratio trenches; alternative deposition methods must, therefore, be developed. One potential technique is plasma-enhanced-chemical-vapor-deposition (PECVD). This technique is especially promising for the deposition of Ta in high aspect ratio trenches because it gives extremely good step coverage and can be done at much lower temperatures than traditional CVD processes. We have successfully deposited high quality Ta films using H2 and TaCl5 in a remote PECVD system. Our Ta films show low levels of impurities and excellent step coverage on patterned Si substrates. Data on deposition rate, conformality, film composition, and electrical properties will be presented.

EM-TuP29 The Characteristics of ZnO:Al Film Using Reactive Magnetron Sputtering System for Touch Screen Applications*, **H.S. Jeong**, M.G. Kim, Y.W. Seo,* ITM Inc., Korea*; S.J. Kwon,* Kyungwon University, Korea

The ZnO:Al (AZO) films deposited on glass for touch screen panels were prepared by in-line reactive magnetron sputtering system. The target materials of magnetron sputtering system were ceramic ZnO:Al@sub2@O@sub3@ and metallic Zn:Al targets. We applied the dc-pulsed power to the targets with the change of duty ratio. To compare the AZO thin film properties with respect to the properties of typical ITO thin film used in touch screen panels, we also prepared ITO films on glass using the in-line reactive magnetron sputtering system and commercial ITO coated glass for touch screen panels. We analyze the electrical and optical characteristics of the AZO and ITO coated glass, and the environmental endurance properties (high-low temperature, temperature/humidity test, etc) of the touch screen panels (4-wire resistive type) made with the AZO and ITO coated glass. The typical range of electrical resistance and optical transmittance of the AZO and ITO coated glass were 400~500@ohm@/Sqr and about 92%, respectively. The electrical and optical properties of the films were measured with a surface profiler, an UV/Visible spectrophotometer, a 4-point probe, X-ray diffraction spectroscopy, and atomic force microscopy. @FootnoteText@ This work was supported by the Ministry of Commerce, Industry and Energy of the Republic of Korea through the National Research Laboratory program.

EM-TuP30 Large Nonlinear Optical Properties of Lead Magnesium Niobate-Lead Titanate Thin Films Grown by Pulsed Laser Deposition*, **D.-R. Liu,*** National Applied Research Laboratories,Taiwan, Taiwan*; P.-T. Cheng,* National Applied Research Laboratories,Taiwan*; S.-L. Ou,* National Taiwan Normal University, Taiwan*; J.-S. Chen,* National Applied Research Laboratories, Taiwan*; C.-P. Cheng,* National Taiwan Normal University, Taiwan

Thin film optical devices have been especially attractive because of their potential for the integration with electronic and optoelectronic systems. Owing to its ferroelectricity, high dielectric constant, and large electro-optic coefficients, Lead magnesium niobate-lead titanate (PMN-PT) can be used in many applications that include pyroelectric detectors, thin film capacitors, nonvolatile memory, and nonlinear optical devices. Because of good transparency over a wide wavelength range of 500nm-7000nm, PMN-PT best suited for almost all the visible to mid IR optical applications. In this study, highly textured thin films of lanthanum doped lead titanate were grown by pulsed laser deposition (PLD) on MgO substrates. The measurement of glancing-angle x-ray powder diffraction (GAXRD) was used to determine the structure of the PMN-PT films. The thickness and roughness of the films were characterized by grazing-incidence x-ray reflectivity (GIXR), and the complex refractive indices were measured in the range from 1.5 to 4.1 eV by spectroscopic ellipsometry (SE). The average oscillator strength and its associated wavelength were estimated by using a Sellmeier-type dispersion equation. Z-scan measurements were performed to study the third-order optical nonlinearity. It was found that the PMN-PT films grown on MgO substrates exhibited strong nonlinear optical effect. The results show that PMN-PT thin films are promising materials for nonlinear optics.

EM-TuP32 Electromigration Performance by Via Structure in Cu Dual-damascene Process*, **H.-K. Lee,** M.-H. Choi,* Chung-Ang Univ., Korea*; N.-H. Kim,* Chosun Univ., Korea*; S.-Y. Kim,* DongbuAnam Semiconductor Inc.*; E.-G. Chang,* Chung-Ang Univ., Korea

In order to improve the interconnect performance, Cu has been used as the interconnect material instead of Al. One of the advantages of using Cu instead of Al interconnects for ULSI circuits is high electromigration (EM) and low resistance and it is based alloys to copper interconnect leads to new via structure fabricated by dual-damascene process. Improved EM characteristic leads to not only high reliability but also high speed of ULSI. The effects of a Ta/TaN Cu diffusion barrier existence on the EM reliability and EM performance of Cu dual-damascene interconnects were investigated. In this study, EM experiments are performed on interconnect structures of via bottom in Cu dual-damascene interconnection system. In result of EM test by interconnect structure, a high EM performance for copper dual-damascene structures was observed with the conventional interconnect structure to remain Ta/TaN barrier layer at via bottom. The failure analysis of the EM investigated with the focused ion beam (FIB), scanning electron microscope (SEM), and transmission electron microscope (TEM) equipments. Failures in direct contact via (DCV) structure by using bottomless process were formed at copper lines. However the EM failures were found at the top of via through the Cu-SiN interface. DCV structure of via EM had lower activation energy than conventional interconnect structure. Via resistance was decreased DCV structure by using bottomless process. The existence of barrier layer at via bottom has the relation with the difference of EM failure mode. From the different via failure modes, it can be concluded that the barrier layer at via bottom was enhanced the back stress in conventional structure due to the blocking of Cu flow. Acknowledgement : This work was supported by grant No. R01-2002-000-00375-0 from the Basic Research Program of the Korea Science & Engineering Foundation.

EM-TuP35 The Growth and Characterization of InN Films Grown by High-Pressure CVD*, **V.T. Woods**, M. Alevli, J. Senawiratne, M. Strassburg, N. Dietz,* Georgia State University

Group III-nitride material systems (e.g. AlN-GaN-InN) have generated considerable interest for use as the basis for advanced opto-electronic device structures. Fabrication of multi-tandem solar cells, high speed optoelectronics and solid state lasers operating in the higher energy wavelengths will be made possible using (Ga@sub1-y-x@Al@suby@In@subx@)N heterostructures due to their robustness against radiation and the wide spectral application range. As organometallic chemical vapor deposition (OMCVD) has proved to be the most efficient technique for commercial production of group III-V semiconductors, it would be expedient to gain insight in applying OMCVD to group III-nitride material systems. However, the growth of indium rich (In1-xGax)N thin films utilizing OMCVD has been unsuccessful, primarily due to the large thermal decomposition pressures in indium rich group III-nitride alloys at the optimum growth temperature. As shown in this contribution, high-pressure chemical vapor deposition (HPCVD) overcomes the limitations, enabling the growth of InN and indium rich group III-nitride alloys. This high pressure approach allows InN growth at temperatures of 1100K and above which is a major step forward towards the production of indium rich heterostructures, providing a closer match to the ideal processing temperatures of (Ga@sub1-x@In@subx@)N. Real-time optical characterization techniques are applied to study and control the gas phase kinetics and surface chemistry processes during he growth process. The ex-situ analysis of the InN layers indicates that the shift of the absorption edge from 1.85 eV down below 0.6 eV is caused by a series of absorption centers, that appear as the indium to nitrogen stoichiometry varies. This contribution will provide results from the real-time optical characterization of InN and will correlation the process parameter to results obtained by XRD, Raman spectroscopy and optical spectroscopy, in order to asses the film quality.

EM-TuP36 Characteristics of Lanthanum Oxide Prepared using La(iPrCp)@sub 3@ and H@sub 3@O*, **S.Y. No**, D. Eom, C.S. Hwang, H.J. Kim,* Seoul National University, Korea

According to scaling rule, high @kappa@ gate dielectric stack with equivalent oxide thickness (EOT) below 1 nm will be required for sub-0.1µm devices. La-based oxides are attractive candidates for this purpose because of high-@kappa@ value, good interfacial properties, and large band offset against the Si. In this report, we deposited lanthanum oxide thin films using La(iPrCp)@sub 3@ (Tris(isopropylcyclopentadienyl)Lanthanum) and H@sub 2@O. The La precursor and H@sub 2@O were injected alternately and purged by Ar gas between the injections. The deposited films underwent various rapid thermal annealing (RTA), and the property changes were investigated. The deposited films contained carbon impurity less than 1 at.% and showed smooth surface (root mean square roughness< 0.1 nm, ~5 nm film). The electrical properties of deposited films were measured on Pt/Lanthanum oxide/p-Si(100) structure, and small frequency dispersion and hysteresis

(<10 mV) were observed in capacitance vs. voltage measurement. The film structures were observed by high-resolution transmission electron microcopy, and the chemical states of interfacial and upper layer were analyzed by angle-resolved X-ray photoelectron spectroscopy. The film showed amorphous structure even after RTA at 900°C. However, chemical states were altered significantly with a change of valence band offset by the RTA. With optimized RTA condition, capacitance equivalent oxide thickness (CET) below 1.1nm was obtained with fairly reduced positive fixed charge density, and accompanied interfacial reaction lead to a decrease of interface trap density.

EM-TuP37 Zr-doped HfO2 High-k Dielectric with an Inserted HfNx Interface Layer*, **J. Yan**, J. Lu, S. Chatterjee, H.C. Kim, Y. Kuo,* Texas A&M University

Hafnium oxide (HfO2) is a popular high-k gate dielectric candidate. However, HfO2 is easily crystallized at a low temperature, such as < 600C. The effective dielectric constant of HfO2 is lowered due to the formation of a SiOx interface layer. Previously, there are reports that the k value of a high-k film can be increased by inserting a high-k interface layer between the high-k film and silicon substrate.@footnote 1@ In addition, the crystallization temperature of a high-k film can be increased by adding a certain amount of dopant.@footnote 2@ In this paper, authors will report new results on Zr-doped HfO2 films with or without an inserted HfNx interface layer. The leakage current is improved with the doping process as well as the addition of a HfNx interface layer. Other dielectric properties, such as the effective k value, interface density of states, trapped charges, and frequency dispersion, and the final interface layer material properties, such as the bond structure and thickness, of the new high-k gate stack will also be presented and discussed. @FootnoteText@ @footnote 1@ J. Lu, J. -Y. Tewg, and Y. Kuo, Engineering the nm-thick Interface Layer Formed Between a High-k Film and Silicon, MRS Symp. Procs. Integration of Advanced Nanoelectronic Devices - Critical Issues and Solutions, 811, 81-86 (2004).@footnote 2@ J.-Y. Tewg,Y. Kuo, and J. Lu, Suppression of Crystallization of Tantalum Oxide Thin Film by Doping with Zirconium, Electrochemical and Solid-State Letters, 8(1), G27-G29 (2005).

Manufacturing Science and Technology
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Topics in Advanced Manufacturing Poster Session

MS-TuP1 Dip-Pen Nanolithography-Based Fabrication of ZnO Microarrays*, **I. Takahiro**, I. Kaoru, S. Nagahiro, T. Osamu,* Nagoya University, Japan

Zinc oxide (ZnO) becomes one of the most important functional materials with unique properties of the near UV emission, optical transparency, electrical conductivity, and surface acoustic wave. Microarrays and micropatterning of functional ceramic materials are expected to provide various applications for microcircuit fabrication. Patterning and arraying techniques are useful for arranging wiring electrode. Conventionally, ZnO micro-patterns and arrays are fabricated by etching with photoresist like the lithography technique for Si. However, it is difficult to find the suitable etching conditions. To overcome the issue, site-selective growth techniques were recently developed. Dip-pen nanolithography (DPN) is a new promising scanning probe-based technique for fabricating sub-100 nm to many micrometer structures on surfaces, since it is a simple method for directly depositing material from an ink-coated atomic force microscope (AFM) tip onto a substrate with a high spatial resolution. In this study, we demonstrate the fabrication of ZnO microarrays on Au through DPN. An oxidized silicon wafer was coated with a Ti adhesion layer via thermal evaporation, which was subsequently coated with Au. DPN was then used to array ZnO microstructures on these substrates with Zn(NO3)2 solution. AFM-probe used in this study was immersed into the solution for a few minutes. The microstructures of ZnO were observed with field emission scanning electron microscope (FE-SEM).

MS-TuP2 The Dependence of Power Trench MOSFET Processes on Wafer Thickness*, **M. Daggubati**, G. Sim, D. Long, H. Paravi, Q. Wang,* Fairchild Semiconductor

The dependence of trench MOSFET processes on wafer thickness has been studied in detail. In the photolithography process, it was found that the photoresist thickness decreased 30Å when wafer thickness decreased from 675µm to 508µm. This is due to the fact that thinner wafer has less thermal dissipation time i.e. Thinner wafer dissipates heat better and heats up quicker than thicker wafer during baking resulting in more evaporation of the photoresist solvent. Unless compensated for, this change in resist thickness adds to process variation affecting critical dimension (CD) and trench depth control. In the silicidation process, after the rapid thermal processing (RTP), the thinner wafers exhibited a lower resistance and higher silicide stress of 3.23E+10 dynes/cm@super 2@ (compared to thick wafers of 4.60E+09 dynes/cm@super 2@) at the source contact due to the reasons mentioned above. Also, the stress is more uniform across the wafer. The Ti/Si reaction is time and temperature dependent. Higher temperature results in more silicide and the reaction creates a volume reduction that induces stress. The silicide layers on the Si wafers have been analyzed using Z-constrast imaging in transmission electron microscopy (TEM) and energy dispersive x-ray (EDX) profiling techniques. Both Z-contrast imaging and EDX profiling revealed a 50 nm thick TiSi layer on the top of TiSi@sub 2@ layer for the thicker wafers. Whereas, no TiSi layer was found in thinner wafers, but Ti-enrichment in the outer part was sometimes observed. The TiSi layer, especially when it's continuous, can modify the electrical property of the devices. The formation of TiSi layer could be attributed to insufficient Si atoms diffused to the outer layer. Higher temperatures in thinner wafers seem to assist in the removal of this TiSi layer.

MS-TuP5 Optimized Cu Electrochemical Plating considering Pattern Dependency in Dual-Damascene Process*, **H.-Y. Yoo**,* Chung-Ang University, Korea*; N.-H. Kim,* Chosun University, Korea*; S.-Y. Kim,* DongbuAnam Semiconductor Inc.*; E.-G. Chang,* Chung-Ang University, Korea

Since damascene technology announced, Cu metallization using electrochemical plating (ECP) has played an important role in back end of line interconnect formation. In damascene process, the problems related with process integration as well as with each unit process are becoming critical issues. Occurrence of step height (SH) and array height (AH) after Cu plating was closely related with pattern dependencies in Cu ECP and influenced in Cu chemical mechanical polishing (CMP) process. So, Cu plating target thickness in Cu ECP process was required to be optimized. In this work, we studied the optimized copper thickness in Cu ECP. In order to select an optimized Cu ECP thickness, we examined Cu ECP bulge (bump, hump or over-plating amount), Cu CMP dishing and electrical properties of via hole and line trench over dual damascene patterned wafers split into different ECP Cu thickness. In the aspect of bump and dishing, the bulge increased according as target plating thickness decreased. Dishing of edge was larger than center of wafer. Also in case of electrical property, metal line resistance distribution became broad gradually according as Cu ECP thickness decreased. In the results, 0.6 @micron@ plating condition that baseline size reduced 40% showed bad property in broad resistance distribution of metal line and dishing after Cu CMP process. In conclusion, at least 20% reduced Cu ECP thickness from current baseline; 0.8 @micron@ and 1.0 @micron@ are suitable to be adopted as newly optimized Cu ECP thickness for local and intermediate layer. Acknowledgement : This work was supported by grant No. R01-2002-000-00375-0 from the Basic Research Program of the Korea Science Engineering Foundation.

MS-TuP7 Fabrication of High Precision Demultiplexer using Embossing Technique with Thermal Curable Polymers*, **C.H. Choi**, M.W. Lee, B.H. O, S.G. Lee,* Inha University, Korea*; S.G. Park,* Inha University, Korea, Korea, Republic of*; E.H. Lee,* Inha University, Korea

Photonic devices have been fabricated mainly by using the conventional lithography and etch processes. However, the costs of the conventional fabrication were remained expensive, and obviously cannot meet the trend towards fiber-to-the-home (FTTH), which required lower price of the photonic components. Embossing technologies reduce the cost for the fabrication of photonic devices. In this paper, we fabricated a 1310 nm/1550 nm demultiplexer using an embossing technique with the PDMS mold. Resists used as the core and the cladding layers are ZP 51 and ZP 49, respectively, which are the thermal curable polymers. The fabrication process is summarized as: 1) manufacturing the photoresist master by lithography process, 2) forming the PDMS mold from the master, and 3) replicating the device using the mold. For the fabrication of the device, ZP 49 was spin coated onto a glass substrate, and was cured by heating. ZP 51 was applied to the patterned surface of the PDMS mold. This mold filled with the ZP 51 was then placed in contact with the surface of the prepared substrate coated the ZP 49, and the ZP 51 was cured to solid by heating it. After curing, the mold was peeled away carefully, and the upper cladding (ZP 49) was spin coated over the patterned structure. The fabrication of the demultiplexer was completed by curing. Some manufacturing issues, such as the variation of dimension of the replica, the durability of the mold, and optical properties of the device, will be discussed. The embossing technique is applied for low-cost manufacturing photonic devices.

MS-TuP8 Silicon Etch for Nano-photonic Structure using Hydrogen Silsesquioxane (HSQ) as a Direct Etch Mask*, **J.K. Kim**, J.H. Sung, K.J. Lim, B.H. O,* Inha University, Korea*; S.G. Park,* Inha University, Korea, Korea, Republic of

As a typical etch process for a Si nano-structure of high aspect ratio requires a bilayer mask or a hard mask, we have investigated the use of a hydrogen silsesquioxane(HSQ) layer as a direct etch mask for Si structure. The HSQ is known as a negative tone e-beam resist good for nanosize patterning. It has attracted lots of attention in the semiconductor industry due to its low dielectric constant, easy processability, good planarization for surfaces, as well as excellent gap fill capability in deep submicron features. In our experiment, thin HSQ layer of 90 nm-thickness was tested as a direct Si etch mask for the etch of sub-micron size hole array of 280 nm in depth and 350 nm in hole-diameter. The etch selectivity of around 2.8:1 for Si to HSQ was obtained so far using SF6-based gas chemistry in our ICP system. The systematic variation of etch parameters were studied to improve the etched wall profile and surface roughness, and the optimized results will be discussed.

MS-TuP9 Mixed Oxidizer Effects on CMP (Chemical Mechanical Polishing) Performance of Nickel for MEMS*, **G.-W. Choi**, N.-H. Kim,* Chosun Univ., Korea*; Y.-J. Seo,* Daebul Univ., Korea*; W.-S. Lee,* Chosun Univ., Korea

Micro electro mechanical system (MEMS) technologies are miniaturized systems which comprise sensor, actuators and electronic functions thereby opening up a whole range of new applications and which would not be possible with purely micro electronic systems. These systems have both electrical and mechanical components. Making small machines which are almost invisible has been one of the dreams of mankind. Nickel and alloys based nickel have been found to have good mechanical properties that can be exploited to realize movable structures in MEMS devices, moreover the magnetic properties of nickel has been widely used in magnetic MEMS. In this study, the effects of oxidants on Nickel with 4 inch diameter and 3 mm thickness chemical mechanical polishing (CMP) process were investigated mixing three different oxidizers such as Fe(NO@sub 3@)@sub 3@, KIO@sub 3@, and H@sub 2@ O@sub 2@ with MSW 2000A slurry. Moreover, the interaction between the Nickel and the oxidizer was discussed by potentiodynamic polarization test with three different oxidizers, in order to compare the removal rate of nickel-CMP and electrochemical corrosion effects on the nickel as a function of oxidizers. As an experimental result, the removal rate of nickel was calculated by measuring the weight loss of the using Shimadzu AEX-300G balance. Fe(NO@sub 3@)@sub 3@ was higher than the other oxidizers. And as concentration in each of oxidizers increased, removal rate also increased, but over the amount, it decreased. Therefore, we conclude that nickel-CMP performances are strongly dependent on the kinds of oxidizers and the amounts of oxidizer additive. Acknowledgement: This work was supported by a Korea Research Foundation grant (KRF-2004-005-D00007).

Nanometer-Scale Science and Technology
Room Exhibit Hall C&D - Session NS-TuP

Nanometer Scale Science and Technology Poster Session

NS-TuP1 Free-standing Nanosheets from Cross-Linked Biphenyl Self-Assembled Monolayers*, W. Eck,* Universtät Heidelberg, Germany*; A. Küller, M. Grunze,* Universität Heidelberg, Germany*; B. Völkel, **A. Gölzhäuser**,* Universität Bielefeld, Germany

Self-assembled monolayers composed of biphenyl units are cross-linked by electron irradiation. These monolayers can be released from the underlying surface by dissolution of the substrate or by scission of the anchor group-substrate bonds. This way, free-standing nanosheets with the thickness of a single molecule and lateral dimensions in the micrometer range are obtained. Gold nanoparticles have been deposited on the sheets and successfully imaged by electron microscopy suggesting their use as substrates for microscopy applications.

NS-TuP2 Pulse Thermal Processing of FePt Thin Films*, **A.C. Cole**, G.B. Thompson,* University of Alabama*; R.D. Ott,* Oak Ridge National Laboratory*; J.W. Harrell,* The University of Alabama

The L1@sub 0@ phase of FePt is a candidate material for next generation magnetic storage because of its high magnetocrystalline anisotropy. When FePt is sputter-deposited onto an ambient temperature substrate, it adopts a metastable solid-solution face-centered-cubic phase that is superparamagnetic. A subsequent anneal is required to chemically order FePt into the L1@sub 0@ phase with its superior magnetic recording properties. A consequence of conventional annealing is grain growth in the film, which is detrimental to increasing areal storage density. We report the use of multiple pulsed-thermal-processing with a high density infrared plasma light source at exposure times of 100 and 250 ms to chemically order FePt films. Upon ordering, no grain growth of the 15 nm diameter columnar grains was observed in 100 nm thick specimens. As the thin film thickness was decreased, grain growth became more prevalent for similar processing conditions. Moreover, for the smaller grain sizes, we observed a strong evolution of texture upon ordering. The morphology of the films pre- and post- processing has been characterized using high-resolution TEM and XRD. Magnetrometry of the samples has also been performed. The results of this work will address the consequences of pulsed-thermal-processing on phase and morphological stability at the nanometer-scale.

NS-TuP3 Etch of Sub-Micron High Aspect Ratio Holes in a Bilayer of SU-8/PMMA Resist Stack for Photonic Crystal Devices*, **J.H. Sung**, K.J. Lim, B.H. O,* Inha University, Korea*; Y.H. Choe,* LG Electronics Institute of Technology, Korea

Sub-micron hole array in a bilayer of SU-8 for core and poly-methyl-metacrylate (PMMA) for clad have been successfully etched for the fabrication of photonic crystal (PC) structures. In the PC waveguides, the etched holes need to be extended into the cladding layer to ensure the proper optical characteristics. The fabrication started from coating multiple materials on a glass substrate to form a multi-layer of hydrogen silsesquioxane (HSQ)/PMMA/SU-8/PMMA. Using a nano-patterned stamp, PC patterns are imprinted into the top HSQ layer at room temperature. After the pattern transfer by a dry etch in our inductively coupled plasma (ICP) system, Cr sputtering was followed for a lift-off process. The Cr pattern was successfully formed on the top of 1-um-thick SU-8 and 2-um-thick PMMA resist stack. Using this Cr pattern as a hard mask, sub-micron holes are etched also in the ICP etcher. Various gas chemistries are attempted to achieve vertical profiles and a high aspect ratio. The best etch conditions for a PC structure with high aspect ratio and vertical side-wall profile will be discussed.

NS-TuP4 An Innovative Approach to Nanoscale Device Fabrication*, **E.A. Akhadov**, A.H. Mueller, M.A. Hoffbauer,* Los Alamos National Laboratory

A recently developed technology exclusive to LANL, called Energetic Neutral Beam Lithography/Epitaxy (ENABLE), offers exceptional opportunities for producing nanoscale structures and for synthesizing thin film materials. ENABLE utilizes reactive neutral atomic species (O and N) having kinetic energies comparable to chemical bonds strengths (a few eV) for etching very high-aspect-ratio features into polymers and for growing oxide and nitride thin films at low temperatures. Using energetic oxygen atoms, numerous nanoscale structures have been fabricated into polymer films that contain sub-100 nm features with very high aspect ratios (in some cases >35:1). For example, using a nanosphere-defined mask a polyimide film was etched to form a periodic array of 5.4 micron tall, 250 nm diameter pillars. As a novel application, nanoscale polymer templates can be fabricated and used for growing nitride (AlN, GaN, etc.) and oxide (Al@sub 2@0@sub 3@, SiO@sub 2@, etc.) structures. This novel fabrication approach can easily be expanded to make 2- and 3-dimensional structures and devices with multiple functionalities. The latest results utilizing ENABLE for producing photonic crystals, MEMS and NEMS devices, microfluidic channels, and novel electronic devices will be discussed.

NS-TuP5 Compositional and Structural Characterization of Tungsten Nanostructures Produced by Electron Beam-Induced Deposition*, **K.L. Klein**,* University of Tennesse & ORNL*; S.J. Randolph, P.D. Rack,* University of Tennessee*; M.L. Simpson,* University of Tennessee & ORNL

Electron beam-induced deposition (EBID) is an emerging technique for the synthesis of nanostructures and nanopatterning. The high degree of precision associated with EBID, (i.e. precise location, size, and shape) makes it a prime candidate for a wide variety of applications ranging from fiber tips for field emission sources to lithography mask repair strategies. Furthermore, a wide array of materials - as governed by the choice of precursor gas - can be deposited by EBID, thus adding to the versatility of the technique. As is the case with all deposition processes, it is critical to be able to control the composition and structure of the deposited material by varying simple process parameters. Thus far there has been very little characterization of the chemical composition and internal structure of EBID materials. Previous results have suggested a significant incorporation of impurities into the deposited material. The deposition conditions as well as precursor composition can impact the resulting chemical composition and nanostructural properties of the deposit. In order to better control these deposit properties, we report on the effects of beam energy, beam current, and localized precursor pressure on tungsten nanostructures deposited by EBID from a tungsten hexafluoride precursor. The results of high resolution TEM, STEM, and EDS on as-deposited tungsten nanostructures will be reported. In addition, the effects of post-deposition processes, such as thermal treatments will be discussed.

NS-TuP6 Formation of Nanometer-scale Structures Based on a Plasma Ashing and Lift-off Technique*, G.-S. Kim,* Sungkyunkwan University, Korea*; Y.-H. Roh,* Sungkyunkwan University, Korea, Republic of Korea

Realization of nano- and/or bio-electronic devices requires the formation of nanometer-scale structures. Recently the fabrications of structures with a nano gap dimension have been demonstrated by using advanced techniques such as electron-beam lithography, focused ion beam lithography, or advanced optical lithography. However, these techniques are very slow, and moreover require a high production cost. Recently, our group proposed the new technique to overcome a resolution limit of an optical lithography for forming nanometer-scale structures. The technique utilizes a well known and a well established processing technique known as a photoresist (PR) ashing. In this technique, the minimum linewidth can be formed by ashing the PR pattern defined by the conventional optical lithography. In this work, we further developed this technique to form the various shapes of nanometer-scale structures including the line-and-space pattern and nanometer-scale holes. In this particular case, we used a negative PR (PMER) instead of a conventionally used positive PR since the final patterns of PMER after treating the ashing process result in the high aspect ratio, reversal echelon formation and excellent property for fine pattering in general. In turn, the lift-off step that is required to form the highly aligned nanometer-scale structures can be easily followed. Based on the current investigation, we found that various types of nanometer-scale structures can be easily formed using semiconductor, metal and insulator materials. These results may open the possibilities to fabricate the unique tools for the vertical-type field effect transistors and highly aligned emitters.

NS-TuP7 Si Nanoclusters Embedded in SiO@sub 2@ Layers Produced by Reactive RF Sputtering*, E. Sanchez-Meza,* ESFM-IPN, Mexico*; **A. Garcia-Sotelo**, M. Melendez-Lira, A. Mendoza-Galvan, S. Jimenez-Sandoval,* Cinvestav-IPN, Mexico

The production of silicon nanonoclusters is an active topic of research because the possibility to produce efficiently light on a silicon based material. We have taken advantage of the morphologic characteristics of the films deposited by the sputtering technique to produce silicon nanoparticles. We have grown silicon nanoclusters embedded in SiO@sub 2@ layers employing reactive RF sputtering. Different partial pressures of Ar/O@sub 2@ were employed to produce the plasma, a 99.999 % pure silicon disk was employed as target. Samples were deposited on substrates of silicon (100) and commercial glass at 400 °C. Samples were characterized by X-ray diffraction, atomic force microscopy and room temperature infrared, ellipsometry, photoluminescence and Raman spectroscopies. X ray diffractograms shown that samples grown on silicon present a crystalline structure while films grown on glass are amorphous. Atomic force microscopy shown in both cases the presence of ellipsoidal mounds with axis lengths around 100 nm. Raman spectroscopy presents Raman shifts located at 470 cm@super -1@ due to Si-nanoclusters. Ellipsometry results indicated, in good agreement with the growth procedure, that sample structure correspond to a a-Si+c-Si layer of around 10 nm embedded in layers of SiO@sub 2@. Our results shown that reactive sputtering has a good potential to produce, at low cost, uniform nanoclusters. @FootnoteText@ @footnote 1@work partially funded by CONACyT-México.

NS-TuP8 Recent Lithography Results from the Digital E-beam Array Lithography (DEAL) Concept*, W.L. Gardner,* *L.R. Baylor,* Oak Ridge National Laboratory*; X. Yang,* University of Tennessee*; R.J. Kasica, D.K. Hensley,* Oak Ridge National Laboratory*; S.J. Randolph, R.B. Rucker, D.C. Joy, P.D. Rack, S. Islam, B. Blalock,* University of Tennessee

The Digital E-beam Array Lithography (DEAL) concept is currently under development at Oak Ridge National Laboratory (ORNL). This concept incorporates a digitally addressable field emission array built into a logic and control integrated circuit to function as the write head for a massively parallel e-beam lithography tool. Each field emission device comprises three electrodes separated 1 µm from each other by SiO2. The first electrode functions as the cathode and contains a single vertically aligned carbon nanofiber as the field emitter. The second is an extraction aperture and the third is an aperture functioning as an electrostatic focusing lens. Field emission and focusing tests on prototype devices demonstrated that the emission follows Fowler-Nordheim characteristics, the beams can be focused as anticipated from numerical simulations, and the extraction and focus apertures in well-aligned devices collect less than 1% of the emitter current. Preliminary lithographic results on PMMA coated substrates demonstrated that variations in linewidth measured as a function of the focus lens voltage are in agreement with device modeling. Recently, we obtained the capability to fabricate thick electrodes, which, based on model results, should provide better focusing and depth of field. Furthermore, progress has been made to obtain better aperture alignment and fabricate individually addressable cathodes. Our research objective is to demonstrate lithography using a full 3x3 array of operating devices. We will discuss our recent results in detail as well as ongoing work to achieve <100-nm linewidths and full array implementation.

NS-TuP9 Characteristic of Carbon Nanotubes Synthesized by Pin-to-Plate Type Atmospheric Pressure Plasma Enhanced Chemical Vapor Deposition at Low Temperature*, S.-J. Kyung,* *J.H. Lee, C.-W. Kim, M. Voronko, G.Y. Yeom,* Sungkyunkwan University, Korea

In this study, carbon nanotubes (CNTs) were grown on glass substrates coated with NiCr by an atmospheric pressure plasma enhanced chemical vapor deposition and their structural and electrical characteristics were investigated as a possible application to the field emitter of field emission display (FED) devices. NH3 gas flow rate (150sccm~ 270sccm) in He/C2H2/NH3 and the substrate temperature (400~500ï,°C) were varied and the increase of NH3 flow rate to 270sccm and the increase of growth temperature to 500ï,°C increased the length of the grown CNTs and decreased the diameter of the CNTs. The ratio of defective carbon peak to graphite carbon peak of the CNTs grown at 500ï,°C with 270sccm of NH3 measured by fourier transform(FT)-Raman was 0.772. When field emission properties were measured, the turn-on field was 3.5V/um and the emission field at 1mA/cm2 was 5.25V/ um.

NS-TuP10 A Method of Coating and Implanting Carbon Nanotube with Iron Nanoparticles by Inductively Coupled Plasma*, J.S. Kim,* *G.H. Kim, C.I. Kim, O.J. Yoon, J.K. Jung,* Chungang University, Korea

We describe a new method of coating and implanting Single-Walled Carbon Nanotube with Iron Pentacarbonyl(FeCo@sub 5@) using Inductively Coupled Plasma(ICP). We control the pressure of chamber by hydrogen gas. First, Iron Pentacarbonyl(FeCo@sub 5@) in bubbler was evaporated by heating. Second, Plasma treatment process was performed with hydrogen gas and the evaporated Iron Pentacarbonyl(FeCo@sub 5@), at rf-bias voltage. The result of this work shows Fe nanoparticles coated and implanted on Single Walled Carbon Nanotube(SWCNT). The morphology and structure was investigated by scanning electron microscopy (SEM), transmission electron microscory(TEM), and energy dispersive x-ray(EDX).

NS-TuP11 Carbon Nanotube Copolypeptide Bionanocomposites*, C. Lovell,* University of Virginia*; E. Worthington,* University of California, Santa Barbara*; T.J. Deming,* University of California, Los Angeles*; G.D. Stucky,* University of California, Santa Barbara*; J. Kang, K.E. Wise,* National Institute of Aerospace*; J.S. Harrison,* NASA Langley Research Center*; J.M. Fitz-Gerald,* University of Virginia*; C. Park,* National Institute of Aerospace

Due to their helical structures, several biopolymers exhibit high shear piezoelectricity. Unfortunately, few natural biopolymers exhibit adequate physical properties to endure practical utilization of their sensing capabilities. Thus, this investigation seeks to explore the shear sensing potential of a synthetic biopolymer. By combining peptides and polymers, synthetic polypeptides should bridge the gap between expensive, functional peptides and inexpensive, less functional polymers. Further augmentation of their electroactive potential and mechanical properties can be achieved by addition of carbon nanotubes (CNTs) to form a nanocomposite material with very low density . Functional characterization of drop-casted thin films was performed, including electrical and dielectric measurements, as well as mechanical tests. It was found that several properties, including conductivity, permittivity, tensile strength, Young's modulus, and toughness increased with SWNT loadings. However, one of the main limiting factors in achieving the best performance of CNT-polymer composites is a sharp increase of material viscosity at high concentrations (5-6 wt.%) of CNTs, which limits the capabilities of conventional fabrication techniques. In order to exploit the unique properties of CNTs in macroscopic composites, significant progress has to be made in the development of new advanced fabrication and processing methods, allowing control over spatial distribution and alignment of CNTs in the matrix. For this reason, a novel process termed "matrix assisted pulsed laser evaporation" (MAPLE) was used in creating several CNT-copolypeptide nanocomposites. These results, as well as the preliminary investigation of the copolypeptide's shear piezoelectric properties, will be presented. @FootnoteText@ @footnote 1@ S. B. Sinnott and R. Andrews, Carbon nanotubes: synthesis, properties, and applications, Crit. Rev. Sol. State Mat. Sci. 26, 145, 2001.

NS-TuP12 Double-walled Carbon Nanotubes Grown on Co Tip Catalysts by Chemical Vapor Deposition*, **C.-M. Yeh**, C.-J. Huang, M.-Y. Chen, J.C. Hwang,* National Tsing Hua University, Taiwan, R. O. C.

A cobalt tip structure has been used as the catalysts for the grown of double-walled carbon naotubes (DWCNTs) by catalytic chemical vapor deposition at 900~1000°C. The cobalt tip catalysts were fabricated by a pre-deposition of a cobalt thin layer of 0.5~10 nm on Si(100) and a sequential microwave plasma treatment at 450°C. The outer and inner tube diameters of the DWCNTs are in the range of 3~4 and 2~3 nm, respectively, determined by transmission electron microscopy. The density of DWCNTs can be enhanced by the Co tip catalysts, which structure is superior to ball-like Co islands for the growth of CNTs.

NS-TuP13 Oxide Electrolyte Nanostructures for Low Temperature SOFC Operation*, **S. Thevuthasan**, L. Saraf, V. Shutthanandan, O.A. Marina, C.M. Wang, S. Azad, Y. Zhang, A. El-Azab,* Pacific Northwest National Laboratory

Development of electrolyte materials that possess high oxygen ion conductance at relatively low temperatures is essential to improve the performance of electrochemical devices. Ceria, doped with a divalent or trivalent cation, exhibits higher ion conductance compared with yittria-stabilized zirconia, the electrolyte currently used in solid oxide fuel cells. In this research, we have investigated layer by layer structures of highly oriented gadolinia doped ceria and zirconia in order to determine the nanoscale effects on the ion conductance. Highly oriented multilayered nanostructures of gadolinia-doped ceria and zirconia with interfaces parallel and perpendicular to the substrate surfaces were grown on sapphire substrates using molecular beam epitaxy and glancing angle sputter deposition, respectively. These structures were characterized by several bulk and surface sensitive characterization techniques. At relatively low temperatures, the oxygen ion conductance in highly oriented layered structures was found to increase with increasing number of layers in the films with interfaces parallel to the substrate surfaces. Theoretical calculations were also performed to understand the effects of space charge regions induced by the thermodynamic equilibrium and impurity segregation as well as the influence of the grain microstructures on the electric transport processes in these materials. In addition, labeled oxygen diffusion measurements were carried out by 18O(p,alpha)15N nuclear reaction analysis (NRA) and the diffusivity correlation is established with ionic transport by measuring the oxygen ionic conductivity using impedance spectroscopy. These results will be discussed along with the results from stability tests of these layered structures at elevated temperatures.

NS-TuP14 Hydrogen Effects on the Field Emission of Carbon Nanostructures*, **P. Miraldo**, R.A. Outlaw, X. Zhao, J.J. Wang, B.C. Holloway,* College of William & Mary

Field emission from carbon nanostructures such as carbon nanotubes (CNT), carbon nanofibers (CNF) and carbon nanosheets (CNS) is greatly influenced by the presence of hydrogen adsorbed on the surface and dissolved in the bulk. The amount and site location of the hydrogen and how it affects electron emission has, to date, not been determined. Temperature desorption spectroscopy, electron energy spectroscopy and time of flight-secondary ion mass spectrometry were employed to examine some of these characteristics. Hydrogen was desorbed from CNS via vacuum firing (T~ 1000@degree@C for 2h for full depletion) and via thermal conditioning at emission currents of greater than 500 uA for periods of 30 min to > 2h. Following conditioning of the CNS, there was a marked improvement in the repeatability, stability and magnitude of the field emission current. Field emission was observed to increase by over an order of magnitude corresponding to the complete removal of hydrogen from CNS. Turn on voltages less than 0.8 V/@micron@ and current densities greater than 2 mA/mm2 have been observed. Raman spectroscopy performed on the CNS after conditioning revealed a significant reduction in the D/G ratio. Comparisons to the reported decrease in electron emission with hydrogen removal from CNT are presented.

NS-TuP15 Fabrication of Three-Dimensional Nanostructures with a Resolution of 10 nm and Selective Attachment of Biological Molecules using Scanning Near-field Photolithography*, **R.E. Ducker**, M. Montague, G.J. Leggett,* University of Sheffield, UK

Scanning near-field photolithography (SNP) is a new nanolithography tool in which a scanning near-field optical microscope (SNOM) coupled to a UV laser is used to pattern organic monolayers. Here we present a detailed study of the mechanism of formation of nanostructures in self-assembled monolayers (SAM) of alkanethiols adsorbed on gold surfaces. A novel mild etch solution has been developed that can be used to selectively etch gold using a SAM resist. Used in conjunction with SNP this enables the fabrication of structures in gold that are smaller than 10 nm using light with a wavelength of 244 nm. In contrast to electron beam methods, SNP may be used under ambient or even fluid conditions. SNP can also be used to create biological nanostructures via a variety of methods.

NS-TuP16 Metal Nanostructure Growth on Molecular Buffer Layers of CO@sub 2@*, **P.S. Waggoner**, J.S. Palmer, V.N. Antonov, J.H. Weaver,* UIUC

Buffer-layer-assisted growth (BLAG) occurs when a multilayer of condensed gas acts as the surface on which impinging atoms form clusters that subsequently diffuse and coalesce during buffer desorption. We investigated Au, Cu, and Ni nanostructure formation using buffer layers of solid CO@sub 2@ and compared the results to what has been found for solid Xe buffers. The cluster densities could be controlled from ~10@super 8@ to 10@super 12@ cm@super -2@ by taking advantage of the power law dependence of density on the buffer layer thickness. For Au and Cu, the crossover from compact to ramified structures could be followed. For Ni, even small particles were ramified. The effective activation energies for diffusion of large ramified clusters on CO@sub 2@ were determined to be 0.91, 1.02, and 0.93 eV for Au, Cu, and Ni, respectively. These were significantly higher than observed on Xe, and they reflect the higher polarizability of CO@sub 2@. The diffusion pre-factors increased exponentially with the increase in diffusion barrier, demonstrating a Meyer-Neldel compensation effect. The characteristic energy of this process, 9 meV, was higher than for Xe due to the more energetic phonons of CO@sub 2@. It is comparable to the energies of buffer phonons active during buffer desorption, revealing that cluster motion on CO@sub 2@ is a many-body process fueled by coincidence of activated buffer phonons.

NS-TuP17 Synthesis of Aligned Carbon Nanotubes by CVD Using Ball-Shaped Microwave Plasma*, **Y. Oshiro**, S. Nishino, Y. Hayashi,* Kyoto Institute of Technology, Japan

Aligned carbon nanotubes (CNTs) have been successfully synthesized by plasma-enhanced chemical vapor deposition using ball-shaped microwave plasma in a quartz bell jar. CNTs are expected to be used as field electron emitters for a display or an X-ray source, because they have the characters of high aspect ratio, small radius of tip curvature and mechanical strength, which are required for long-lived emitters with intensive electric field at their tips even at low applied voltage. Ball-shaped microwave plasma, which is generated non-contact with a quartz bell jar, has been used for aligned CNTs growth because of high purity CNT synthesis. In the plasma, CNTs are expected to grow in an environment with few impurity inclusion by the sputtering of the wall of a quartz bell jar. 10% methane diluted in hydrogen was introduced in the bell jar chamber and the pressure was kept at 2000 Pa during the growth of CNTs. Microwave power of 450W was induced for the generation of ball-shaped microwave plasma. For the growth of vertically aligned CNTs, we placed a DC cathode plate parallel to a grounded electrode , which plays a role of an end plate for microwave propagation, to apply a uniform and intensive electric field on a substrate. Iron substrates were set on the cathode plate, to which negative bias of 300V was induced. Aligned carbon fibers of 30 nm in diameter and 800 nm in length were observed by scanning electron microscopy. These carbon fibers should be CNTs formed by tip growth, because they were hollow and had cone-shaped particles at their tips, which are generally observed to be those of iron catalytic metal in the tip-growth mode of CNTs.

NS-TuP18 Arrayed Bundles of Carbon Nanotubes for High-Intensity Field Emission: Parametric Studies of Growth and Field Emission*, **M.J. Bronikowski**, H.M. Manohara, B.D. Hunt,* Jet Propulsion Laboratory, California Institute of Technology

We have found that Carbon Nanotubes (CNT) arranged in arrays of bundles give much greater field emission current densities that either isolated CNT or dense mats of CNT, in excess of 1 Amp/cm^2 at fields of less than 4 Volts/micron. As part of ongoing efforts to fabricate high-intensity electron-beam devices based on these arrayed CNT bundles, we have studied CNT bundle growth (by Chemical Vapor Deposition, CVD) as a function of the various CVD processing parameters, and field emission intensity as a function of CNT bundle array geometric parameters such as bundle size, spacing, and CNT length and diameter. Results will be presented from these parametric studies, in which we have optimized both CNT growth and field emission of electrons from arrayed bundles of CNT.

NS-TuP19 Suspended Carbon Nanotube Electro-Mechanical Tunneling Switch for Wireless Communication*, **Y. Song**, J. Choi,* Wayne State University

Carbon nanotube is one of the best building blocks for future nano electro-mechanical systems especially in wireless communication application. It is originated from the excellent properties of carbon nanotubes such as high mechanical strength, chemical inertness, high aspect ratio, and good thermal conductivity. We directly fabricated laterally suspended carbon nanotube tunneling switch and studied its characteristics and performance as an electro-mechanical switch. The onset of tunneling turn-on voltage of carbon nanotube switch is as low as 2.6 V. The switching behavior of carbon nanotube electro-mechanical switch was modulated by a back gate voltage and investigated by in-situ Raman spectroscopy and impedance spectroscopy.

NS-TuP20 Experimental Evidence of p-type Doping for Long Channel Carbon Nanotube Transistor*, **D. Kang**,* Samsung Advanced Institute of Technology, Korea*; N. Park,* Dankook University, Korea*; B. Kim, J. Kim,* Chonbuk National University, Korea*; W. Park,* Samsung Advanced Institute of Technology, Korea

Carbon nanotubes(CNT) show dramatic changes in physical and chemical properties under different ambient conditions because of its high surface area. However, the possibility of p-type doping has been controversial for several years. While the thermoelectric power measurement obviously reported the oxygen-induced hole doping in the bundles of nanotubes, transport measurement with single short nanotube revealed that the adsorption effect lead to the work function change of the electrode, rather than the doping the nanotube body. However, in this study, we show that the doping effect would be prominent in the single nanotube transistor when the CNT is long(~5 µm). In order to decouple mixed effects from doping and metal work function change, we masked the interface (CNT/metal) and channel (CNT) region of CNT FET with conventional photoresists, respectively and measured Ids-Vg characteristics in air and vacuum. Preliminary data show that p-doping due to adsorption of ambient gas molecules could be possible and another critical factor to govern electrical properties of long channel CNT transistors. In addition, we observe that changes in Ids-Vg and Vth (threshold voltage) are associated with where it was masked.

NS-TuP21 Electrical Properties of a Silicon Nanocrystal Embedded in a SiO2 Layer*, **J.M. Son**, J.M. Kim, S.Y. Seong,* Myongji University, Korea*; Y. Khang, B.K. Kim, K.S. Seol, E.H. Lee, J. Lee,* Samsung Advanced Institute of Technology, Korea*; Y.S. Kim, C.J. Kang,* Myongji University, Korea

Si nanocrystal (Si NC) based device is a promising candidate for the future non-volatile memory. It is advantageous in terms of low power consumption, small device size, excellent stress induced leakage current (SILC) immunity and better retention. Since the characteristics of Si NCs memories in which the conventional poly-Si floating gate is replaced by an array of Si NCs is affected by the electrical properties of each NC, the isolation of Si NCs plays an important role. The Si NC samples produced by laser ablation method were followed by sharpening oxidation steps. In these steps Si NCs are capped with a thin oxide layer of 1~2nm thickness for isolation and the size control. It also affects the interface states of NCs, resulting in the change of electrical properties. To find out this effect, we observed localized electrical properties of a capped Si NC by scanning probe microscopy (SPM). And these results were compared with C-V characteristics of the conventional MOS capacitor structure.

NS-TuP22 Synthesis of Carbon Nanofibers on TiW Substrates and Their Field Emission Properties*, **K. Hou**, J.J. Wang, P. Miraldo, R.A. Outlaw, B.C. Holloway,* College of William and Mary

Spaghetti-like and aligned carbon nanofibers have been synthesized on TiW substrates by DC PECVD at a substrate temperature of 635°C. The morphology transition from spaghetti-like to aligned carbon nanofibers has been observed to be a function of plasma power. It is found that the growth rate plays an important role in determining the morphology of carbon nanofibers. When the growth rate is less than 150 nm/min, aligned carbon nanofibers can be fabricated. Otherwise, spaghetti-like carbon nanofibers are formed. The growth rate of carbon nanofibers fabricated on TiW substrate at 550°C is also measured in this work. The field emission properties of both spaghetti-like and aligned carbon nanofibers grown on TiW substrate at 635°C have also been investigated.

NS-TuP23 Temperature-induced Control of the Aspect Ratio of Gold Nanorods*, H.J. Park, C.S. Ah,* Korea Research Institute of Standards and Science*; K.-P. Lee,* Kyungpook National University, Korea*; I.S. Choi,* KAIST, Korea*; **W.S. Yun**,* Korea Research Institute of Standards and Science

Aspect ratio of gold nanorods can be controlled by simply adjusting the reaction temperature in the seed-mediated synthesis of the nanorods. At various reaction temperatures between 276 and 313 K, the gold nanorods were prepared by the injection of gold nanoparticles of around 4 nm in diameter into a reaction mixture consisting of hydrogen tetrachloroaurate, hexadecyltrimethylammonium bromide, and ascorbic acid. Average aspect ratio of the resulting nanorod increases from 1 to about 40 with decreasing the reaction temperature, which can be attributed to temperature-induced change in the stability of the micellar templates.

NS-TuP24 Controlled Gold Nanowires using 2-Aminoethanthiol Capped Gold Nanoparticles on DNA Molecule as Template*, **H. Kim**, B. Hong,* Sungkyunkwan University, Korea*; Y.-H. Roh,* Sungkyunkwan University, Korea, Republic of Korea

We developed a simple technique to form Au-nanowires (AuNWs) by the conjugation of 2-aminoethanthio-capped gold nanoparticles (AET-AuNPs) and the immobilized DNA molecules on 3-Aminopropyltriethoxysilane (APS) coated Si wafers. The AuNPs coated with AET monolayers have been electrostatically assembled along DNA molecules by careful control of the relative molar quantities of AuNPs and AET. We carried out a variety of AuNPs sizes (2, 5, 10 nm) to form the various nanowires, and the various sizes of nanowires were achieved. The gold nanowires formed in this study were confirmed by atomic force microscopy (AFM). In addition, we measured an electrical conductivity of AuNWs located between microfabricated electrodes. The investigated nanowires exhibit ohmic transport behavior at room temperature.

NS-TuP25 Synthesis and Characterization of SiC Nanowires and SiC/ZnO Hetero-Nanostructure Grown by Direct Heating Method*, **Y. Ryu**, Y. Tak, K. Yong,* POSTECH, Korea

SiC is a suitable material for the fabrication of electronic devices operating at high power, high temperature and high frequency due to its unique physical, mechanical and electronic properties. Cubic phase SiC nanowires were synthesized in large quantity by simply heating NiO catalyzed Si substrates at the growth temperature of about 1050 @super o@C. A carbothermal reduction of WO@sub 3@/C provided reductive environment and also carbon source to synthesize crystalline SiC nanowires. SiC nanowires were 20-50 nm in diameter, and the as-grown nanowires were coated with SiO@sub 2@ sheath of ~ 20 nm thick. The grown nanowires were characterized using SEM, TEM, EDX, Raman spectroscopy, FTIR and XRD. Also, the electron field emission properties of the SiC nanowires and core-shell SiC-SiO@sub 2@ nanowires were investigated. The turn on field at the emission current density of 10 µA/cm@super 2@ was below 4 V/µm, and it showed uniform emission image. Hetero-nanostructure of ZnO nanorods(NR)/SiC nanowires(NW) were produced using a two step process: direct growth and metal-organic chemical vapor deposition (MOCVD). Atomically abrupt interface was observed at the heterojunction of ZnO NR/SiC NW. The photoluminescence (PL) of aligned ZnO nanorods will be discussed as well.

NS-TuP27 Formation of Ge Nanocrystals in Hf based High-K Dielectrics for Nonvolatile Flash Memory Device Application*, J. Chen,* National University of Singapore*; A.-Y. Du,* Institute of Microelectronics, Singapore*; **W.J. Yoo**,* National University of Singapore, singapore*; D.S.H. Chan,* National University of Singapore

Nanocrystals (NCs) floating gate has received considerable attention for the future nonvolatile flash memory devices because its discreteness of charge storage suppresses lateral migration of charges, enhancing immunity to oxide defects compared with conventional flash memories using continuous floating gates. High-K dielectrics in place of conventional SiO@sub 2@ can further improve programming efficiency, data retention and read speed of flash memory because of lower F-N tunneling barriers and small equivalent oxide thicknesses. In this work, methods to form Ge nanocrystals embedded in main stream high-K dielectrics, HfO@sub 2@ and (HfO@sub 2@)@sub x@(Al@sub 2@O@sub 3@)@sub 1-x@ (HfAlO) were introduced and compared. Temperature dependence of phase separation process in the formation of Ge NCs in HfO@sub 2@ and HfAlO matrices was studied using X-ray photoelectron spectroscopy. Transmission electron microscopy and energy dispersive X-ray spectroscopy show that

Ge NCs can form in either HfAlO or HfO@sub 2@, and the location of Ge NCs varies depending on the high-K films. It is found that, in HfAlO, Ge NCs are well sandwiched in amorphous HfAlO matrix. However, in HfO@sub 2@, Ge NCs are located in grain boundaries of polycrystalline HfO@sub 2@, and most of Ge NCs are in direct contact with Si substrate or gate electrode of memory devices because of the extrusion effect of the growth of HfO@sub 2@ crystal grains on Ge NCs. This results in a significant difference in data retention of memories employing these structures. Flash memories employing Ge NCs embedded in HfAlO can maintain a memory window of 0.5 V in 10 years, whereas flash memories employing Ge NCs embedded in HfO@sub 2@ show a memory window closing only within 2 minutes.

NS-TuP28 Electrical Characteristics of DNA-Nanoparticle Networks using Scanning Probe Microscopy*, N.J. Lee*, *Y.J. Kim, J.S. Kim, B.H. Nahm,* Myongji University, Japan*; D. Jeon,* Seoul National University, Korea*; Y.S. Kim, C.J. Kang,* Myongji University, Korea

Transport properties of the DNA-nanoparticle networks constructed by the self-assembly of biotinylated DNAs and streptavidins are studied by scanning probe microscopy (SPM). First, we measured I-V characteristics of DNA network linked between two metal electrodes deposited on mica surface, and these results were classified with respect to the conformational change of DNA molecules. Next, SPM probe tip was used as a counter electrode for the fixed metal electrode. In this experiment, only one end of DNA molecule was attached to the fixed electrode and the tip was scanned over DNA molecules to measure the local property. We also monitored capacitance or potential difference within the networks with SPM while biasing the network. To find out the charging effect in the network, we directly injected charge into the DNA molecule through SPM tip and performed microscopy and spectroscopy. In this talk, local electrical properties of the DNA-nanoparticle networks observed by SPM and their possibility to be applied for nano devices will be presented.

NS-TuP29 Observation of Broad Strong Red Photoluminescence Band in Indium Oxy-nitride Nanoparticles*, T.S. Ko*, *C.P. Chu, W.T. Hsu, H.C. Kuo, S.C. Wang,* National Chiao Tung University, Taiwan

Indium oxy-nitride nanoparticles were synthesized on silicon substrate in nitrogen atmosphere using a method involving thermal evaporation of pure indium. Nanoscale compositional analysis by energy dispersion spectrum showed the existence of indium oxy-nitride compound. Scanning electron microscopy investigations showed shape transformation from amorphous sphere to well-shaped octahedron with an average nanoparticle size from 180 nm to 1 µm when growth temperature of substrate increased from 700 to 900 °C. Photoluminescence study was performed on indium oxy-nitride nanoparticle samples grown at different temperatures. It was found that all of samples grown at different temperatures exist a broad emission band centered around 690 nm with a full width at half maximum is about 250 nm, spanning the whole red region. The emission intensity increases with growth temperature, which suggests the formation of high quality indium oxy-nitride nanoparticles with increasing temperature. The photoluminescence results indicate the indium oxy-nitride nanoparticle samples have potentialities of developing into red phosphor system for lamp applications.

NS-TuP30 Single-Crystal GaN Nanorod Arrays Grown by UHV RF-MOMBE*, C.N. Hsiao*, *C.-C. Kei,* National Applied Research Laboratories, Taiwan*; C.K. Chao,* National Central University, Taiwan*; S.-Y. Kuo,* National Applied Research Laboratories, Taiwan

Well-aligned GaN nanorod arrays have been grown by ultra-high vacuum metal organic molecular beam epitaxy using RF radical nitrogen (RF-MOMBE) on c-sapphire substrates without any catalyst. The corresponding microstructure and growth kinetics of rods were investigated by in-situ reflection high-energy electron diffraction, scanning electron microscopy, transmission electron microscopy, energy dispersive spectroscopy, x-ray diffraction, micro-Raman spectroscopy, photoluminescence and high resolution transmission electron microscopy (HRTEM). It was found that the length and diameter of nanorods varies with the growth temperatures, and the rod number density can reach around 10@super 10@ cm@super -2@. HRTEM and corresponding diffraction patterns have revealed the GaN nanorods have a dislocation free, single-crystal hexagonal wurtzite structure with preferential (0001) orientation. However, the selected area electron diffraction patterns (SADPs) for the interface were not clear enough to identify corresponding orientation relationship between rod and substrate. Further research about growth mechanism is still needed in this area. The findings in this work show that the size and density of the rods can be controlled by adjusting the III/V ratio, RF plasma power and growth temperature. In contrast to previous works, the process requires neither catalyst nor the effect of nanometer-sized confinement such as carbon nanotubes. Thus, the single-crystal and dislocation-free GaN nanorods arrays might be useful for practical applications in nanoscale optoelectronic and electronic devices.

NS-TuP31 ZnXCd1-XSe Ternary Semiconductor Nanoalloys*, H. Lee*, *L. Hardison, H. Yang, V.D. Kleiman, P.H. Holloway,* University of Florida

ZnxCd1-xSe quantum dots have been synthesized by a high temperature colloidal method using a trioctylphosphine oxide (TOPO) solution. Oleic acid complexes of Cd and Zn were used for the metal sources in reactions that produced ZnxCd1-xSe nanoalloys. Nanoalloying was achieved during the one-step synthesis process that led to a ZnSe shell on the CdSe core. Reaction temperatures below 250oC led to less alloying and less spectral shifts as compared to dots synthesized at 320oC. Smaller nanocrystals were obtained at lower growth temperature due to a smaller critical radius of nucleation, leading to a large nucleation rate. ZnCdSe nanorods were also synthesized from CdSe/ZnSe coreshell nanorods via a solution thermal alloying process at 270~280oC. CdSe nanorods were prepared using tetradecylphosphonic acid (TDPA)/TOPO surfactants, and a ZnSe shell was grown on CdSe nanorods at 180~190oC. These nanorods were characterized as a function of alloying time using X-ray diffraction, Raman, transmission electron microscopy, and time-resolved photoluminescence spectroscopy. Femto-second transient absorption in the visible emission spectra was used to study the alloying mechanism(s). The decay of luminescence in ZnxCd1-xSe nanoalloys is best fit by stretched-exponential function and the significance of this observation will be discussed.

NS-TuP32 The Dependence of Photoluminescence Characteristics of In2O3 Nanowires on the Zn Doping Level*, C.L. Hsin*, *J.H. He, L.J. Chen,* National Tsing Hua University, Taiwan, R.O.C.

Nano-scaled materials have attracted increasing attention because of their novelty and potential applications. In this paper, we report the growth of In2O3 nanowires with different zinc doping levels in the vacuum furnace by a vapor transport and condensation method. The photoluminescence properties were measured and discussed Self-assembled indium oxide nanowires with different zinc doping levels have been synthesized on the silicon wafer in a vacuum furnace. The morphologies, structures and chemical compositions have been studied by field emission scanning electron microscopy and transmission electron microscopy. The photoluminescence properties of the samples were measured at room temperature. The presence of metal particle at the top indicates that the growth of the nanowire is by VLS mechanism. The intensity variation with the doping level of the samples can be seen clearly. The band diagram can explain the photoluminescence characteristics. The photoluminescence properties are attributed to the radiative recombination between oxygen vacancies, zinc impurities and indium-oxygen vacancy pairs.

NS-TuP33 Synthesis of One-dimensional Well-aligned ZnO Nanorods on Patterned Structures*, C.W. Wang*, *J.H. He,* National Tsing Hua University, Taiwan, ROC*; L.J. Chen,* National Tsing Hua University, Taiwan, ROC., Taiwan, R.O.C.*; G.C. Wu, C.T. Chia,* National Taiwan Normal University, Taiwan, ROC

The synthesis of one-dimensional (1D) semiconducting oxide nanomaterials has drawn a great deal of attention. ZnO has a wurtize structure with applications in catalysts, sensors, actuators and transducers. Under controlled conditions, 1D well-aligned ZnO nanorods are synthesized by a simple vapor transport via vapor-liquid-solid (VLS) process on patterned single crystal (11-20) sapphire. The patterning methods include atomic force microscope-tip induced technique and nanosphere lithography. From FESEM images, ZnO nanorods are vertically aligned on the substrate and have uniform diameter of about 100 nm. From TEM images, ZnO nanorods are single crystal and grown along c-axis. Photoluminescence measurements show that a peak occurs at 380 nm which is attributed to band edge emission.

NS-TuP34 Amorphous Nanotubes by Self-Assembly of Amphiphilic Bi(hexadecylamine) Zinc Sulfato Complex with Size Tunability*, G.W. Huang*, *J.H. Wang, H.C. Chen,* National Tsing Hua University, Taiwan, Republic of China*; L.J. Chen,* National Tsing Hua University, Taiwan, Republic of China, Taiwan, R.O.C.

We describe on the formation of amorphous (C@sub 16@H@sub 33@NH@sub 2@)@sub 2@ZnSO@sub 4@ nanotubes based on directional buttom-up self-assembly process. Through catalytic chemical reaction, the bi-hexadecylamine coordinated zinc sulfato complex is generated as a long-period molecular chain. The nanotubes were analyzed by FTIR, ESCA and line-scan EDX analysis to confirm the nanotubes are composed of (C@sub 16@H@sub 33@NH@sub 2@)@sub 2@ZnSO@sub 4@ complex. The zinc coordinated bi-hexadecylamine provides a multiple intermolecular hydrophobic interaction and drives these molecular backbones to be close together. The as-bulit nanotubes were identified through analytical electron microscope observations, which reveal the nanotubes possess outer diameters of 60-90 nm and on inner diameter of 20 nm with length up to several micrometers. Additionally, through stoichiometry adjustment the length could be reduced drastically to hundreds of nanometer. The tunability in length is also reflected from photophysicical properties with size-dependent optical characteristics. Further molecular packing profile revealed by small angle X-ray scattering strongly suggests and sustains the long range ordering (ca. 3.99 nm d-spacing) within these nanotubes.

NS-TuP35 Formation of Ordered Nanodots with Si-Ge Superlattices by One Step Etching Process*, **H.C. Chen**, S.W. Lee,* National Tsing Hua University, Taiwan, Republic of China*; L.J. Chen,* National Tsing Hua University, Taiwan, Republic of China, Taiwan, R.O.C.

Semiconductor superlattices are attracting increasing attention due to their potential applications in thermoelectric and optoelectronic devices. While the 2-dimensional (2D) semiconductor possesses promising properties for optoelectronic devices such as light emitting diode, heterostructure formation in zero-dimension (0D) nanostructure may provide even more attractive characteristics and improve device performance. By the use of comparably low etching-rate and size uniformity of Ge QDs, a method was developed to fabricate nanodots with excellent uniformity over large area, containing Si-Ge superlattices structure. The density of the nanodots is about 1*10@super 10@ /cm@super 2@, equivalent to that of original Ge QDs. Pyramid-like nanodots containing Si-Ge superlattices with 35 nm in height and 80 nm in diameter have been successfully fabricated. The use of Ge QDs/Si-Ge superlattices heterostructure takes advantages of not only Ge QDs with good size uniformity and low etching-rate to obtain nanodots with Si-Ge superlattices structure, but also compatible with the Si/SiGe-based integration technology.

NS-TuP36 Synthesis of Au Nanotubes with SiO@sub x@ Nanowires as Sacrificial Templates*, **M.Y. Lu**, Y.C. Chang,* National Tsing Hua University, Taiwan, ROC*; L.J. Chen,* National Tsing Hua University, Taiwan, ROC, Taiwan, R.O.C.

Gold nanotubes with SiO@sub x@ nanowires as sacrificial templates have been synthesized. SiO@sub x@ nanowires were functionalized by 3-aminopropyl trimethoxysilane (APTMS) that generates a charged surface. The attachment of negatively charged gold nanoparticles was followed. The coverage of Au nanoparticles was initially less than 30 percents. Further coverage was achieved by the reduction of gold hydroxide to grow the continuous nanoshell on Au nanoparticles, which serve as nucleation sites. The final coverage of gold nanoshells on SiO@sub x@ nanowires depends strongly on the relative amount of SiO@sub x@ nanowires in gold hydroxide solution. TEM images showing the progressive growth of gold shells on SiO@sub x@ nanowires decorated with Au nanoparticles. FESEM image shows the open ends of Au nanostructures after etching by HF solution confirming the formation of Au nanotubes by a simple route.

NS-TuP37 Orientation Controlled Growth of Epitaxial SiNWs Networks in Ar Ambient*, **H.W. Wu**, H.C. Chen,* National Tsing Hua University, Taiwan, ROC*; L.J. Chen,* National Tsing Hua University, Taiwan, ROC, Taiwan, R.O.C.*; C.J. Tsai,* National Tsing Hua University, Taiwan, ROC

Epitaxial silicon nanowire networks have been synthesized with a convenient annealing process in Ar ambient. Au nanoparticles were used as catalysts for nanowire synthesis via the vapor-liquid-solid growth mechanism. From the SEM observation, silicon nanowires form rectangular networks on (100) Si, and parallel straight lines on (111) Si. The diameters of silicon nanowires are between 10 and 60 nm. Structural characterization showed that the silicon nanowires grow primarily along the directions. The heights of silicon nanowires are between 3 and 20 nm. For applications in nanotechnology, growing silicon nanowires epitaxially on a suitable substrate promises to realize a high density of integrated devices based on nanowires.

NS-TuP38 QCM Studies of the Slippage of Solid and Liquid Krypton Monolayers on Metal(111) and C60 Surfaces*, **T. Coffey**, J. Krim,* North Carolina State University

We report a Quartz Crystal Microbalance (QCM) study of the nanotribology of solid and liquid krypton monolayers adsorbed on Cu(111), Ag(111), Ni(111), and C60 substrates at 77.4 K. We document the liquid-solid phase transition and compare the slip times of the krypton for the various substrates. The slip times for the solid krypton monolayers are longer than the slip times for liquid krypton monolayers on metal substrates and monolayer C60 films, as observed previously for krypton/Au(111). However, for bilayer C60 films, the jump in slip time at the liquid-solid phase transition is not present. We discuss these topics and the underlying reasons.

NS-TuP39 Nanotribological Effects of Silicone Type and Deposition Level and Surfactant Type on Human Hair using Atomic Force Microscopy*, **C.A. LaTorre**, B. Bhushan,* The Ohio State University

The atomic/friction force microscope (AFM/FFM) has recently become an important tool for studying the micro/nanoscale structure and tribological properties of human hair. Of particular interest to hair and beauty care science is how common hair care materials, such as conditioner, deposit onto and change hair tribological properties, since these properties are closely tied to product performance. Since conditioner is a complex network of many different ingredients (including silicones for lubrication and cationic surfactants for static control and gel network formulation), studying the effects of these individual components can give insight into the significance each has on hair properties. In this study, AFM/FFM is used to conduct nanotribological studies of surface roughness, friction force, and adhesive force as a function of silicone type, silicone deposition level, and cationic surfactant type. Changes in coefficient of friction as a result of soaking hair in de-ionized water are also discussed.

NS-TuP40 Morphological, Nanomechanical and Cellular Structural Characterization of Human Hair and Conditioner Distribution Using Torsional Resonance Mode with an AFM*, B. Bhushan, **N. Chen**,* The Ohio State University

Characterization of cellular structure and chemical and physical properties of hair are essential to develop better cosmetic products and advance the biological and cosmetic science. Although the morphology of the fine cellular structure of human hair has traditionally been investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), atomic force microscopy (AFM) can be used for characterization in ambient conditions without requiring specific sample preparations and surface treatment. In this study, tapping mode (TM) and torsional resonance (TR) mode in an AFM are compared for measurements of stiffness and viscoelastic properties mapping of the materials using amplitude and phase angle imaging. The TR mode shows advantages in resolving in-plane (lateral) heterogeneity of materials. The TR mode has been used for investigating and characterizing fine cellular structure of human hair. Various cellular structure (such as the cortex and the cuticle) of human hair and fine sublamellar structures of the cuticle, such as the A-layer, the exocuticle, the endocuticle, and the cell membrane complex could be easily identified. The distribution and thickness of conditioner on treated hair surface affects tribological properties of hair. The conditioner thickness has been estimated using force distance measurements with an AFM.

NS-TuP41 Atomic-scale Studies of Friction and Nano-Indentation*, **T. Filleter**, S. Maier, R. Bennewitz,* McGill University, Canada*; E. Meyer,* University of Basel, Switzerland

The development of Scanning Force Microscopy has provided us with tools to study friction and wear on the nanometer scale. The characteristic atomic stick-slip instability in friction force measurements is caused by the jump of the contacting tip from one atomic position to the next. Thermal fluctuations in the combined system of tip, surface, and force sensor play an important role for the development of the stick-slip behavior. We measured the friction force for atomic stick-slip friction of a nanometer-sized tip sliding on a KBr (100) surface in ultra-high vacuum. Our friction force microscope allows us to detect force fluctuations up to 3 MHz, well above the mechanical resonance of the force sensor. We could track thermal fluctuations and found that the duration of the slip event shows a broad distribution even for slips over neighboring atomic positions. The indentation of surfaces by sharp tips is a standard method used to determine hardness and elastic modulus of materials. Scaling these experiments to small lengths can probe the initial stages of permanent deformation. Atomic scale plastic deformation at crystal surfaces has been achieved and characterized by use of non-contact force microscopy in ultra-high vacuum. A sharp silicon tip, first implemented as a nano-indenter, was used to image the atomic structure of displaced material on Cu (100) and KBr (100) surfaces. Under nano-Newton loading conditions the debris reorganizes in crystalline terraces with the same orientation as the underlying crystal.

Plasma Science and Technology
Room Exhibit Hall C&D - Session PS-TuP

Plasma Science and Technology Poster Session

PS-TuP1 Aluminum Nitride formed by Expanding Thermal Arc Plasma Chemical Vapor Depositon*, **G.T. Dalakos**, H. Marek,* GE Global Research Center

This work involves very-high deposition rates of aluminum nitride thin films using a novel, high-density expanding plasma source to dissociate suitable gas-phase precursors. The plasma source is produced from a DC thermal arc discharge that expands into the vacuum deposition chamber, breaking up gas feedstock and forming film precursors. Due to the large, charged species concentration present in the arc source, use of this plasma source allows us to achieve unusually large deposition rates of a few microns/min. In this regard, we discuss the differences between our approach and conventional deposition approaches. We additionally discuss how experimental processing parameters of the expanding thermal arc source affects measured film properties such as composition, morphology and crystalline nature of our deposited films.

PS-TuP2 Study of Deposition Precursors in Amorphous Silicon Nitride Film Deposited by Plasma CVD*, **Y. Ichikawa**, M. Narita,* Fuji Electric Device Technology, Japan*; S. Fujikake,* Fuji Electric Advanced Technology, Japan

To understand the deposition mechanism of hydrogenated amorphous silicon nitride film (a-SiN:H) deposited by plasma CVD, we have studied the deposition precursors and their effective sticking coefficient both in SiH@sub 4@-NH@sub 3@ and SiH@sub 4@-N@sub 2@ gas mixture systems. The a-SiN:H films were deposited on a silicon wafer where a number of trenches with a width of 1µm were formed by etching, and then their film thickness profiles and composition on the trench wall were measured. These experimental results were compared with Monte-Carlo simulation to estimate the species of precursors and their vanishing probability on the deposition surface. The results showed that in SiH@sub 4@-NH@sub 3@ system the dominant precursor is one species (with a vanishing probability of 0.08) and the composition of the film does not vary along the trench wall. On the other hand, in SiH@sub 4@-N@sub 2@ system two species have to be taken into account to fit the simulation with experimental results; one species has a vanishing probability of 0.8 and the other has that of 0.05. Moreover, the composition of the film varies along the trench wall; the ratio of nitrogen to silicon increases with increasing distance from the surface in a trench.

PS-TuP3 Deposition of SiOxNy Films by PE-CVD for OLED Passivation*, **J.H. Lee**, C.H. Jeong, J.T. Lim, J.H. Lim, S.-J. Kyung, G.Y. Yeom,* Sungkyunkwan University, Korea

To prevent the permeation of H@sub 2@O and O@sub 2@ to the devices, the encapsulation of the devices such as metal encapsulation and glass encapsulation are currently used for OLED devices, however, thin film passivation instead of the encapsulation on these devices are preferred for the lighter weight, wider viewing angle, flexibility, etc. Therefore, various permeation barrier materials and various deposition methods for these materials are intensively investigated for the passivation of the next generation flexible flat panel display (FPD) devices such as OTFTs and OLEDs. In this study, bis(tertiary-butylamino)silane (BTBAS) was used as the precursor of Si, SiO@sub x@N@sub y@ thin films were deposited on plastic substrates at a low temperature using a PECVD method and its properties were investigated. BTBAS was used as the precursor of Si because it shows a low impurity content after the deposition and it is safe, easy to handle as a liquid form, and chemically stable compared to other silicon precursors such as SiH@sub 4@, SiH@sub x@Cl@sub y@, etc. Also, by forming multiple layers of SiO@sub x@N@sub y@/parylene, the water permeation properties of the deposited SiO@sub x@N@sub y@ films were also investigated. In this presentation, we will report the deposited film characteristics for an OLED passivation layer such as deposition rate, film crystallization, chemical composition, H@sub 2@O permeation, and optical transmittance measured using an alpha-step, XPS, FT-IR, ellipsometer, and UV spectrometer, respectively.

PS-TuP4 Linearized Process Model Analysis As a Means of Understanding the Behavior of the Reactive Sputtering Process*, **D.J. Christie**,* Advanced Energy Industries, Inc.

Reactive sputtering processes exhibit unique control space behavior which has been effectively explained by mathematical models. The reactive gas partial pressure can have multiple possible values for a range of reactive gas flows which leads to hysteresis in the process control space. A model which effectively explains the process dynamics consists of three coupled non-linear differential equations. Jacobian linearization of the model equations can be used to create a linearized model whose eigenvalues can be determined explicitly.@footnote 1@ Evaluation of the linearized model eigenvalues as a function of reactive gas partial pressure shows the specific partial pressures where hysteresis is likely to occur. In this work, a representative reactive sputtering process is modeled. The small (control) signal analysis and stability are correlated to the reactive gas partial pressure and flow characteristics. In particular, the real and imaginary components of the eigenvalues and the reactive gas flow are evaluated for a realistic range of reactive gas partial pressures. The points where hysteresis is expected to occur based on the two approaches (flow versus pressure, eigenvalues versus pressure) are compared. Insights on process dynamics and potential closed-loop control issues are also extracted from the linear analysis. @FootnoteText@ @footnote 1@ C. Li, J-H Hsieh, Surface and Coatings Technology 177-178, 824 (2004).

PS-TuP6 Stabilization of the Atmospheric Glow Plasma*, **E. Aldea**, P. Peeters,* Eindhoven University of Technology, The Netherlands*; H. de Vries,* Fuji Photofilm B.V*; M.C.M. Van De Sanden,* Eindhoven University of Technology, The Netherlands

*****PLEASE NOTE: YOU MUST IDENTIFY A DIFFERENT PRESENTER FOR THIS ABSTRACT. YOU MAY ONLY PRESENT ONE (1) PAPER AT THE CONFERENCE.*****Due their huge potential for cost efficient industrial applications uniform atmospheric plasmas (atmospheric glow) attracted a lot of interest in the recent years. Commonly atmospheric glow plasma can be straightforwardly generated only in He or very pure nitrogen and at relatively low power density. It is widely believed that atmospheric glow generation is related to a large pre-breakdown pre-ionization but the link between pre-ionization and atmospheric glow remains debatable. In this paper it is argued that not the pre-ionization but thermal/ionization instability is the key factor, which is preventing the atmospheric glow generation. Excepting He atmospheric plasma generation requires the suppression of the unstable plasma modes. In this way we succeeded to generate the atmospheric glow at high power density and for a large variety of gases. Several dedicated electronic circuits were developed for the suppression of the unstable plasma varieties. The plasma stabilization electronics is exploiting the peculiar low ratio of the dynamic to static resistance of the unstable plasma varieties.

PS-TuP8 Frequency and Dimensional Scaling of Microplasmas Generated by Microstrip Transmission Lines*, **I. Rodriguez**, J. Hopwood,* Northeastern University

A microplasma is generated in a gap formed between the ends of a microstrip transmission line. The microstrip is fabricated in the shape of a circular ring, and the discharge gap is micromachined through the microstrip such that the device resembles a nearly closed C. This geometry resonates if microwave power is coupled to the split-ring at a frequency for which the circumference is one-half of the wavelength. At resonance, a strong electric field is generated in the discharge gap region and a microplasma may be ignited. Split-ring resonator microplasmas operating at 900 MHz have been reported in the literature@footnote 1@ and operate from 0.1 Torr to 760 Torr in air as well as inert gases. The primary advantage of this device in comparison to low frequency and DC microplasmas is the elimination of ion-induced erosion of the micro-electrodes. The ions are not accelerated toward the electrodes because the split-ring is at a constant DC potential. In addition, the ions cannot respond to the microwave field. In this presentation, we report scaling the split-ring resonator. Using an aluminum oxide substrate (@epsilon@@sub r@ = 10.2), the 900 MHz device must be 20 mm in diameter. By increasing the operating frequency to 1.8 GHz, the split-ring resonator is scaled down to approximately 10 mm. Higher frequency operation also improves the confinement of the electrons within the discharge gap by decreasing the amplitude of electron oscillation. The scaled split-ring resonator operates in argon at 1 atm using 0.3 watts supplied by a power amplifier chip from a cell phone. Electromagnetic simulations and measurements of the physical device compare favorably@footnote 2@. @FootnoteText@ @footnote 1@F. Iza and J. Hopwood, IEEE Transactions on Plasma Science, Vol. 31(4), pp. 782-787 (2003).@footnote 2@This work is supported by NSF Grant No. CCF-0403460.

PS-TuP9 Effect of Gas Flow on the Gas Temperature in a High Pressure DC Micro-discharge*, **F. Doll**, Q. Wang, V.M. Donnelly, D.J. Economou,* University of Houston*; G.F. Franz,* University of Applied Sciences, Germany

The gas temperature of a high pressure DC micro-discharge in mostly Ar or He was deduced by spectroscopic measurements of the rovibrational bands of the second positive system of N2, added as a trace species. The micro-discharge was sustained in a slot between two molybdenum electrodes separated by a distance of 200 microns. The gas temperature in He was significantly lower (350-550 K) than that in Ar (over 1000 K), a reflection of the much higher thermal conductivity of He. Increasing the gas flow rate had little effect on the gas temperature in He, but significantly reduced the gas temperature in Ar. This is consistent with the fact that conductive heat losses dominate in the helium micro-discharge, while heat losses by convection play a role in the Ar micro-discharge. The experimental findings were verified with a two-dimensional flow and heat transfer calculation in the micro-plasma reactor. Finally, the cathode temperature was measured with a thermocouple located 1 mm from the face of the electrode exposed to the plasma. The cathode temperature in the Ar micro-discharge was generally less that 400 K. Work supported by DoE/NSF.

PS-TuP10 Plasma-Deposited Silver Containing Nanocomposite Coatings with Bactericidal Properties*, **P. Favia,*** University of Bari, IMIP-CNR, Plasma Solution Srl, Italy*; E. Sardella, M. Nardulli,* University of Bari, Italy*; R. Gristina,* Institute of Inorganic Methodologies and Plasmas (CNR-IMIP) Bari*; R. d'Agostino,* University of Bari, IMIP-CNR, Plasma Solution Srl, Italy

Silver has been considered for centuries for its antibacterial properties,@footnote 1@ that are explained with different mechanisms, including strong interactions with thiol groups of the respiratory enzymes of bacteria. Silver has a broad spectrum of action, from anaerobic bacteria to viruses, yeasts, and fungi. The overuse of silver compounds causes argyria, a discoloration of the skin, often due to the uptake of improperly prepared and unstable colloidal silver. For this reason the interest is often focused on products for topical therapies@footnote 2,3@ instead of systemic, able to release in a controlled way the minimum quantity of silver effective. Nanocomposite coatings (i.e. dispersions of Ag clusters embedded into an organic/inorganic matrix) are under investigation in our lab as silver delivery systems, as alternative to available medical products, since they allow to control the release rate of silver as a function of their chemical composition.@footnote 4,5@ In this work the attention is focused on the ability of such coatings to release a minimum quantity of silver in cell-culture medium without losing bactericidal effect. Coatings have been deposited in RF (13.56 MHz) Glow Discharges fed with a mixture of Diethyleneglycole di-methyl ether (DEGDME) and Ar. Sputtering from the Ag-coated cathode of the reactor occured simultaneously in certain conditions, to give Ag clusters dispersed in the Polyethyleneoxide (PEO)-like coating. Different PEO-like and Ag/PEO-like coatings have been deposited, that have been characterized with different surface analysis techniques. The role of silver and its cytotoxycity in cell culture media has been evaluated with 3T3 Murine Fibroblasts at different time of incubation. The bactericidal effect of Ag+ ions was evaluated with different bacteria. Biological results have been correlated with the quantity of silver released in water at 37°C, as measured with ICP Emission spectroscopy. Acknowledgements: The project MIUR-FIRB RBNE01458S_006, is gratefully acknowledged for funding this research @FootnoteText@ @footnote 1@ Russell et al, Hugo. Antimicrobial Activity and Action of Silver. Prog Med Chem. 1994, 31:351;@footnote 2@ Thomas et al, J Wound Care 2004; 13(9):392;@footnote 3@ Dowling et al, Thin Solid Films 2001; 398-399: 602;@footnote 4@ Favia et al, Plasmas and Polymers 2000, 5(1):1;@footnote 5@ Sardella et al, Plasma Proc. and Polym., 2004, 1:63.

PS-TuP13 Functionalization of Rough Polymer Surfaces and Porous Micron-Sized Beads Using Atmospheric Pressure Plasmas@footnote 1@*, **A.N. Bhoj,*** University of Illinois at Urbana-Champaign*; M.J. Kushner,* Iowa State University

Pulsed atmospheric pressure plasma discharges, such as corona and dielectric barrier discharge devices, are commonly used to functionalize surfaces (e.g., polymer sheets) with the advantages of high throughput and in-line continuous processing. These materials have surface roughness of 100s nm to 10s µm often resulting from the manufacturing process. Porous materials also have highly non-planar surfaces that can be functionalized for novel applications such as drug delivery. In this paper, results from a computational multiscale investigation of atmospheric pressure plasma treatment of rough polymer surfaces and porous polymeric beads are discussed. The investigation was conducted with a 2-dimensional plasma hydrodynamics model using an unstructured mesh capable of resolving a dynamic range of 1000 in spatial scale.@footnote 2@ This capability enables a multi-scale approach in which the reactor scale plasma hydrodynamics and penetration of plasma produced species into surface structures can be simultaneously addressed. A surface kinetics model is integrated with the plasma hydrodynamics model to assess the uniformity of treatment of the surface structures. The model geometry is a dielectric barrier-corona configuration at atmospheric pressure with a gap of a few mm to the surface. Nitrogen-containing gas mixtures produce amine functionalities on rough polymer surfaces and porous polymer beads of 10s µm sizes with pore diameters less than 2 µm. Radicals and ions generated in the plasma diffuse through the pores and access the internal surfaces, a process that depends on polarity of the corona. The uniformity of treatment of the nooks-and-crannies of the rough surfaces and on the internal surfaces of the polymer beads depends on the relative rates of transport and reaction limited processes, and evolves over successive pulses as the surface functionalization is saturated. @FootnoteText@ @footnote 1@ Work supported by NSF (CTS03-15353). @footnote 2@ A. N. Bhoj and M. J. Kushner, J. Phys. D. 37, 2910 (2004).

PS-TuP14 Plasma Simulation for Plasma-based Ion Implantation Sterilization Technique*, **T. Tanaka,*** Hiroshima Institute of Technology, Japan*; M. Tanaka,* PEGASUS Software Inc., Japan*; D. Nakamura,* TWO CELL CO. Ltd., Japan*; H. Fukuyama,* Kobe Steel Ltd., Japan*; T. Takagi,* Hiroshima Institute of Technology, Japan

Plasma-based ion implantation (PBII) sterilization technique is one of the promising sterilization process for three-dimensional work pieces with low temperature, short process time, and no toxic gas. The energy of nitrogen ion used PBII sterilization process with a pulsed negative high voltage (5 usec pulse width, 300 pulses/s, -800 V to -13kV) was estimated using a simple method based on secondary-ion mass spectroscopy analysis of the vertical distribution of nitrogen in PBII-treated Si. The ion energy was calculated based on the depth profile of nitrogen in ion implanted and was low compared to the nitrogen energy calculated based on the voltage applied during processing. It was shown that the experimentally estimated ion energy was at the same level of the value estimated using the plasma simulation. It was shown that the possibility of the design sterilization process and apparatus by using the plasma simulation.

PS-TuP15 Extraction and Collimation of Laser Photoionized Neodymium Ion Beam*, **K.T. Tamura,*** Japan Atomic Energy Research Institute, Japan

Based on the laser isotope separation, ions are produced by the selective photoionization of evaporated atoms. By the effective extraction and collection of these ions, they are considered to be a useful ion source for the applications such as ion implantation. To increase the beam intensity for these applications, a pair of semispherical electrodes was set outside the parallel plate electrodes, and the obtained intensity distributions were measured by scanning a multichannel Faraday cup. Atomic beam of neodymium were generated by electron beam evaporation, and was introduced between electrodes for ion extraction. The atomic beam was photoionized by the irradiation of the third harmonics of YAG laser operated at 10 Hz, and the produced ions were extracted from the electrode. The intensity distributions of the ion beam were detected with a multichannel Faraday cup which has five detection holes arranged horizontally. The distributions were mapped by vertically scanning the detector manually. The vertical and horizontal widths of the ion beam at the detector were reduced by the electric field formed with these electrodes. The central ion beam intensity increased about 36 times compared with that in the case without the additional electric field. The energy spread of the neodymium ion beam corresponded to the potential of the laser photoionized region between ion extraction electrodes. Ions with the central energies of 300~1400 eV were then produced, and it was shown from ion distribution measurements that collimated ion beam was produced for these ion energies. These results show that the application of these electrodes is useful for the extraction and collimation of the laser photoionized ions.

PS-TuP16 Time-Dependent Recombination Reactions of Oxygen Atoms on an Anodized Aluminum Plasma Reactor Wall, Studied by a Spinning Wall Method*, P.F. Kurunczi, **J. Guha,** V.M. Donnelly,* University of Houston

We have studied the pressure, power, and time dependence of recombination of O atoms on an anodized Al surface, using a new "spinning wall" technique. With this method, a cylindrical section of the wall of the plasma reactor is rotated, and the surface is periodically exposed to the plasma and then to a differentially pumped mass spectrometer (MS). By varying the substrate rotation frequency (f), we vary the reaction time, t@sub r@ i.e. the time between exposure of the surface to O-atoms in the plasma and MS detection of desorbing O@sub 2@ (t@sub r@=1/2f). At 600 W and 5 mTorr, the O@sub 2@ desorption signal decreases by a factor of 6 as t@sub r@ is increased from 0.7ms to 40ms. (The signal is zero at f=0.) The O@sub 2@ signal decay rate is highly non-exponential, slowing at longer times. As power is lowered, the signal decreases more strongly at short t@sub r@ than at long t@sub r@. For constant power, signals also decrease at pressures above or below 5 mTorr. The shape of the decay curve is determined solely by the O@sub 2@ desorption signal extrapolated to t@sub r@=0, which is determined by the absolute O flux in the plasma. We have also studied the time dependence of recombination by spinning the substrate at a rapid rate and then turning the plasma on and off. The rate of rise and decay in signal is again highly non-exponential; O@sub 2@ desorption decays by 1/e in ~30ms and is still detectable ~200ms after the discharge extinguishes. When the plasma is turned on, the rise time in O@sub 2@ signal mirrors the decay (~30ms and ~200ms components) if the plasma was recently operated (within the last minute) and is much longer (~2s) if the plasma was off for more than 1 hr, indicating some initial conditioning of the surface. Mechanisms and modeling of O-atom recombination will be compared with these time-dependent results. Supported by ACS-PRF. @FootnoteText@ P.F. Kurunczi - Present affiliation: Varian Semiconductor Equipment, Gloucester, MA 01930.

PS-TuP17 Effect of Coulomb Collision on Oxygen Plasma*, K. Nanbu,* ***T. Furubayashi,*** Tohoku University, Japan

Plasma processing has been used for fabricating semiconductors. The requirement of high aspect ratio etching is satisfied by using low pressure and high density plasmas. When simulating high density plasmas (n@sub e@ = 10@super 17@-10@super 18@m@super -3@), collision between charged particles should also be taken into consideration. Generally, in simulating plasma using the particle model, we consider only electron-molecule collisions and ion-molecule collisions. In this study, we consider not only such collisions but also electron-electron collisions using Bobylev and Nanbu method,@footnote 1@ because it is most probable that Coulomb collision have effect on the electron energy distribution. We examined the effects of Coulomb collision on plasma parameters. Especially, the effect on electron energy distribution function (EEDF) is important because it influences reaction rate of radicals production and hence, affects the etch rate. The effect of electron-electron collisions on argon plasma was examined previously,@footnote 2@ and we found that there is an effect on electron temperature but little effect on the EEDF. In this study, we simulated oxygen plasma using PIC/MC method considering four species, e@super -@, O@super +@, O@sub 2@@super +@, and O@super -@. The threshold energy of ionization in the collisional events of electron-oxygen collision is much lower than that of argon. So it is expected the electron-electron collisions have large effects on plasma parameters. @FootnoteText@ @footnote 1@ A. V. Bobylev and K. Nanbu, Phys. Rev, E, Vol.61(2000), pp. 4576-4586@footnote 2@ K. Nanbu, T. Furubayashi and H. Takekida, Thin Solid Film(to be published).

PS-TuP18 The Role of Ar Metastables in Distorting Gas Temperature Measurements Derived from Trace N@sub 2@ Optical Emission Rotational Spectroscopy in Ar-Containing Discharges*,* ***S.J. Kang,*** *V.M. Donnelly,* University of Houston

Gas temperature (T@sub g@) is an important parameter in plasma prosessing. One method for obtaining T@sub g@ is to add small quantities of N@sub 2@ to the discharge and determine the rotational temperature (T@sub rot@) of N@sub 2@ from electron-impact induced emission. The assumption is that collisions with electrons transfer the rotational distribution of the ground state intact to the emitting state. Usually the 0->0 and 1->0 vibronic bands of the C@super 3@@PI@@sub u@ -> B@super 3@@PI@@sub g@ transition are observed. We have found that when the plasma contains large amounts of Ar these emissions do not yield reliable values for T@sub g@. For example, in a 98% Ar/ 2% N@sub 2@ inductively-coupled plasma (ICP), these bands yield an apparent T@sub g@ that decreases with increasing power. This erroneous result is due to a second mechanism of N@sub 2@ C@super 3@@PI@@sub u@ excitation by collisions with Ar metastables (Ar*). Kinetic modeling shows that at low powers, this Penning excitation mechanism dominates over electron-impact excitation, while at high power, the converse is true. Penning excitation releases a large amount of energy into N@sub 2@ (C@super 3@@PI@@sub u@) rotations. When this process dominates, the observed T@sub rot@ is very high and greatly exceeds T@sub g@. Consequently, T@sub rot@ decreases with increasing power. When N@sub 2@ emission is observed from vibrational levels above that of Ar (@super 3@P@sub 0@) (11.72 eV), i.e., for v' > 4, Ar* energy transfer is no longer possible. So T@sub g@ derived from the 3->3 vibronic band is lower and increases slightly with power. This trend is more reasonable than the high values and inverse dependence on power from the 0->0 transition, consistent with emission from the 3->3 vibronic band arising only from collision with electrons. Thus the 3->3 band provides a reliable measure of T@sub g@.

PS-TuP19 PLAD Dopant Depth Profile Based on Ion Mass and Energy Distribution for Ultra Low Energy Implantation*,* ***L. Godet,*** *S. Walther, S. Radovanov, Z. Fang, J. Scheuer,* VSEA*; G. Cartry, C. Cardinaud,* Nantes University, France

With standard ion implantation technology, the energy and the mass of the ions striking the wafer are well known and simulations such as Transport of Ions in Matter (TRIM)@footnote 1@ are available to predict dopant depth distribution. During the plasma doping process,@footnote 2@ all the ion species present during the negative voltage pulse applied to the substrate are implanted with an energy spread that is dependent on many plasma parameters. To predict the junction depth and the dopant concentration of a plasma doping implant, the knowledge of the chemical nature of the ion species bombarding the wafer, their energy and their proportion of the total ion flux incident on the wafer are needed. In order to provide this essential information, an ion mass and energy spectrometer is installed below the wafer. The ion mass and energy distributions of the ions striking the wafer with energy range from 250V to 1kV have been measured. Secondary Ion Mass Spectrometry (SIMS) was performed to measure the dopant depth profile under the same conditions. Based on the knowledge of the energy distribution of each species of dopant ion present in the pulsed discharge, a TRIM simulation was performed to model the dopant depth profile in the silicon and compared to SIMS profile. @FootnoteText@ @footnote 1@The Stopping and Range of Ions in Solids, J. F. Ziegler,1985@footnote 2@Plasma Diagnostics in pulsed plasma doping system, B.-W. Koo, IEEE, 2004

PS-TuP21 Characteristics of Inductively Coupled Plasma Source with a Multiple U-Type Internal Antenna for Flat Panel Display Applications*,* ***K.N. Kim,*** *C.K. Oh, G.Y. Yeom,* Sungkyunkwan University, Korea

The development of large-area and/or large-volume plasma source with a high plasma density is desired for various plasma processes from microelectronic fabrication processes to flat panel display device fabrication processes. The plasma sources developed to date for the production of high-density and large-area plasmas are mainly focused on the externally planar ICP. However, scaling up to a conventional spiral-type external plasma sources to a large area sources causes some problems when they are applied to TFT-LCD, and by inserting an antenna into the plasma, more production applicable large area ICP is feasible due to the induction of a strong electric field in the plasma and the efficient power transmission to the plasma. In this study, an internal type large-area plasma source with U-type internal linear- antennas has been proposed as a promising candidate for an efficient high-density plasma source. The characteristics of the plasmas were measured using a Langmuir probe located on the sidewall of the chamber. The results showed a strong dependence of the plasma characteristics such as plasma density and plasma uniformity on the antenna arrangement.

PS-TuP22 Electron Density Measurements with Surface Wave Probes in Magnetized Plasmas*,* ***K. Nakamura,*** Chubu University, Japan*; S. Yajima, H. Sugai,* Nagoya University, Japan

In this paper, the surface wave (SW) probe for measuring electron densities@footnote 1@ was applied to magnetized plasmas, and the characteristics of the SW probe located in parallel to the field were examined experimentally and theoretically under a condition of low plasma density and/or high magnetic field corresponding to magnetron discharges. The experiments were made in inductively-coupled argon magnetized plasmas, and absorption frequencies of the SW probe measured by a network analyzer was examined as a function of the plasma frequency measured by the Langmuir probe. At the low magnetic field, the absorption frequency decreased with a decrease in the plasma, thus proportional to the plasma frequency. However, as the magnetic field increased, a saturation of the decrease in the absorption frequency was observed, especially for the low plasma frequency. The saturated absorption frequency were very close to the electron cyclotron frequency obtained from the applied magnetic field, suggesting that the absorption frequency was seriously affected by the magnetic field under the low density conditions. Actually, plotting absorption frequency @omega@ over cyclotron frequency @omega@@sub c@ as a function of plasma frequency @omega@@sub p@ normalized by @omega@@sub c@, its slope approached to zero with an decrease in @omega@@sub p@/ @omega@@sub c@. This result suggested that the absorption frequency became independent of the plasma frequency as a decrease in @omega@@sub p@/ @omega@@sub c@ and that the density measurements was difficult under the low density and/or high field conditions of @omega@@sub p@/ @omega@@sub c@~0.5. Such a saturation was improved by optimization of dimensions of the probe.

Especially, reducing the diameters of the rod antenna and the quartz cover tube of the probe was effective and extended measurable range of @omega@@sub p@/ @omega@@sub c@. @FootnoteText@ @footnote 1@ H. Kokura et al: Jpn. J. Appl. Phys 38 (1999) 5262.

PS-TuP23 Optical Emission Measurements of Dual Frequency Capacitively Coupled Plasmas*, **E.C. Benck,** K.L. Steffens,* National Institute of Standards and Technology

Dual frequency capacitively coupled plasma sources are becoming increasingly important in semiconductor manufacturing processes. By having the two frequencies separated sufficiently far apart, it is possible to essentially independently control the plasma density and ion energies impacting wafers. This significantly increases the operating range and etching control over that of a single frequency CCP. An imaging spectrometer combined with a high speed intensified CCD camera is utilized to obtain spatially and temporally resolved measurements of the optical emissions from dual frequency fluorocarbon plasmas created in a Gaseous Electronics Conference (GEC) reference reactor. Plasma behavior is characterized for a variety of operating conditions. In particular, the influence of a single vs. multiple powered electrodes will be presented.

PS-TuP24 Characterization of an Energetic Neutral Beam Source*, **C. Helmbrecht**, Q. Wang, V.M. Donnelly, D.J. Economou,* University of Houston*; G.F. Franz,* University of Applied Sciences, Germany

The residual ion beam and the energetic neutral beam of a neutral beam source were characterized using an ion energy analyzer in combination with a calorimeter. The beam was extracted through a neutralizer metal grid with high aspect ratio holes separating a 13.56 MHz inductively coupled argon plasma from the differentially-pumped beam characterization chamber. By biasing an acceleration electrode in contact with the plasma, ions in the plasma were expelled through the neutralizer grid, and turned into energetic neutrals by colliding with the internal walls of the holes of the grid. Several Al neutralizer grids were used to study the effect of hole diameter (190-630 microns) and aspect ratio (7:1 and 10:1) on neutralization efficiency and flux. The energy distribution of the residual ions was generally bimodal and the average energy varied in the range of 50-100 eV depending on acceleration voltage and plasma gas pressure. The neutralization efficiency increased with larger holes and higher aspect ratios, approaching complete neutralization of the beam. By assuming that the energy of the energetic neutral beam is approximately the same as that of the residual ion beam, the flux of energetic neutrals was also found. The variation of flux with source operating conditions will be discussed and explained based on plasma molding inside the holes of the grid. Work supported by the Texas Advanced Technology Program.

PS-TuP25 Helicon Discharges with Permanent Magnets*, **H. Torreblanca**, F.F. Chen,* University of California, Los Angeles

Industrial helicon sources have been shown to produce higher plasma densities than unmagnetized ICPs but require the addition of a dc electromagnet and its power supply. This requirement can be obviated by using permanent magnets (PMs). However, injection is a problem, since the field lines of PMs normally do not allow the electrons to leave the source region. Using PMs, we have measured the plasma properties both inside the source and downstream in various helicon discharges, including the Big Blue Mode. To overcome the injection problem, we have tried various types of antennas and various ways to shape the magnetic and electric fields.

PS-TuP26 Discharge Electrode Impedance Effect on Harmonics Generation*, **Y. Yamazawa**, M. Nakaya, M. Iwata, A. Shimizu,* Tokyo Electron AT LTD, Japan

The radio frequency (rf) power is commonly used to excite plasma or biasing the wafer in a plasma reactor for processing of microelectronics materials. Due to the nonlinear behavior of the plasma sheaths, the rf power imposes harmonics of the drive frequency. The generation of the harmonics is of great technological importance, since it contributes significantly to the plasma property and process result. This paper reports the control of the harmonics generation by means of the electrode impedance in a dual-frequency capacitively coupled plasma reactor. The 2nd ,3rd and 4th harmonics of the bias RF frequency were observed to behave with resonant growth by tuning the electrode impedance adequately. A simple nonlinear equivalent circuit model can reproduce the experimental result. A remarkable change in the radial distribution of electron density was observed at the harmonic resonances. This technique can be applied to control the plasma uniformity of the etch chamber. In addition, this technique can be used for reducing chamber-variation by avoiding the unexpected resonance.

PS-TuP27 Electron Beam-Generated Plasmas Produced in Nitrogen and Applications to Materials Processing*, **S.G. Walton**, D. Leonhardt, R.F. Fernsler,* US Naval Research Laboratory*; C. Muratore,* US Air Force Research Laboratory

Electron beam-generated plasmas produced in a nitrogen background have several unique characteristics that make them attractive for materials processing applications that utilize nitrogen species. The US Naval Research Laboratory has developed a plasma processing system that relies on a magnetically collimated, sheet of multi-kilovolt electrons to ionize the background gas and produce a planar plasma. High-energy electron beams are efficient at producing high-density plasmas (n@sub e@ > 10@super 11@ cm@super -3@) with low electron temperatures (T@sub e@ < 0.5 eV) over the volume of the beam, resulting in large fluxes of low-energy ions (< 4 eV) at surfaces located adjacent to the electron beam. Of particular interest to nitrogen-based processing applications are the relative concentrations of atomic ions, molecular ions, and radicals, which are significantly different from other plasma sources. Large atomic-to-molecular ion flux ratios (>1) and radical-to-ion fluxes ratios are possible using simple adjustments to system operation, such as substrate position or plasma duty factor. In this work, we discuss in situ plasma diagnostics of pulsed, electron beam-generated plasmas produced in pure nitrogen and nitrogen mixtures. A Langmuir probe and a dual energy/mass analyzer is used to provide a spatio-temporal description of the processing system. The diagnostic results are correlated to the latest results from materials processing applications under study in our laboratory including metal nitriding, reactive sputter deposition, and polymer modification. This work was supported by the Office of Naval Research.

PS-TuP29 A High Density Negative Ion Plasma in a Very High Dielectric-Constant Discharge Tube*, **Y. Ikeda,*** KYOSERA Co. LTD., Japan*; K. Endo, H. Shindo,* Tokai University, Japan

Negative ions in plasmas are much attractive species in material processing, such as ion implantation, CVD and etching in ULSI fabrications. The objective of this work is to study a negative ion plasma source. In particular, an innovative method to produce a negative ion rich plasmas is proposed by employing RF surface-wave plasma with a extremely high dielectric constant discharge tube. As well-known, the surface-wave can only be existed above the resonance density, which depends on the permittivity of the discharge tube. In this work, a negative ion plasma is produced by employing the after-glow appeared in the resonance density of the surface-wave which is enhanced by a extremely high dielectric constant discharge tube. The surface-wave plasmas of O2 and SF6 were produced in a discharge tube by supplying 13.56 and 60 MHz power. The two discharge tubes of a ceramic of TiCa-TiMg, K-140, which is commercially available from KYOCERA Co. and a quartz are employed, and their permittivities are, respectively, 140 and 3.8. The optical emission line measurements were carried out from the lateral view. The axial decay rate of the intensities of the optical emission lines FI in SF6 plasma were 5 times faster in the K-140 discharge tube than in the quartz. In particular, a sudden precipitation of the line intensity could be observed, and this is due to the surface-wave ending at the resonance density, providing a high density after-glow. In O2 plasma, in this after-glow region, the OI emission lines of 777 and 845 nm, which are originated from the mutual neutralization of O- and O+, were observed to be very much enhanced after the sudden precipitation, indicating the rich negative ions populated in this region. While in the quartz discharge tube the line intensity decayed just simply and monotonically. Thus it was concluded that the surface-wave plasma with a extremely high dielectric constant discharge tube was an innovative method of negative ion rich plasma.

Advanced Surface Engineering
Room Exhibit Hall C&D - Session SE-TuP

Advanced Surface Engineering Poster Session

SE-TuP1 HPPMS Growth of High Sputtering Yield Metallic Films*, S.L. Rohde,* University of Nebraska*; D.J. Christie,* Advanced Energy*; S. Sevvana, S. Chennadi,* ***D.M. Mihut****, J. Li,* University of Nebraska

Ionization levels as high as 70-90% have been reported using High-Power Impulse Magnetron Sputtering (HPIMS),also know as HPPMS, as compared with 5-10% ionization typical in conventional dc magnetron sputtering. Unfortunately, the overall deposition rates observed in most HPPMS studies is significantly lower than (~30%) for conventional dc magnetron sputtering. In the present study, the deposition rate of HPPMS films has been studied as a function of the impulse voltage (or charge voltage). The studies have been carried out for both high sputtering yield metals including Al and Cu, as well as low sputtering yield compounds, such as CrB@sub 2@. While the overall deposition rate increases with increasing impulse voltage or pulse power; this relationship does not follow the same linear relationship observed for dc sputtering. Additionally, under specific conditions it has been shown that dynamic deposition rate [nm/(watt*s)] can exceed that obtained using comparable dc power levels. This trend is observed only for materials with very high sputtering yields, but in all cases there are distinct changes in film properties, such as texture, surface roughness and residual stress, as a function of impulse voltage or power. Other variables considered include: substrate bias, supplemental discharge confinement and angle of inclination. Discussed are some of the implications of and possible explanations for this variation in dynamic deposition rate, making it possible to envision applications were HPPMS techniques might have significant advantages over conventional magnetron sputtering.

SE-TuP2 Low Temperature Deposition of @alpha@-Al@sub 2@O@sub 3@ by Plasma Chemical Vapor Deposition*, **D. Kurapov**, J.M. Schneider,* RWTH Aachen, Germany

Al@sub 2@O@sub 3@ coatings were deposited on tempered hot working steel substrates (X38CrMoV5-1) by plasma enhanced chemical vapor deposition. The influence of the substrate temperature on the constitution of the alumina films was investigated in the temperature range from 500 to 600 °C and normalized ion flux values of 100, 140, 270, and 480. The constitution of the deposited films was analyzed by grazing incidence x-ray diffraction (GIXRD). Additional information about phases formed was obtained from atomic force microscopy (AFM) of polished films. It was found that the phase formation was strongly affected by the normalized ion flux. Alpha Al@sub 2@O@sub 3@ films were obtained at a growth temperature as low as 500 °C. The hardness and elastic modulus of the deposited films were evaluated by nanoindentation. The correlation between deposition parameters and mechanical properties of Al@sub 2@O@sub 3@ films can be understood in terms of the density reduction due to changes of the ion flux. It was found that maximum hardness and elastic modulus values were obtained at low normalized ion flux values.

SE-TuP3 Laser Processing of Crystalline Technologically Relevant Glass-Forming Alloys for Enhanced Corrosion Resistance*, **J.M. Fitz-Gerald**, J.G. Hoekstra, M.A. Jakab, S.J. Poon, G.J. Shiflet, J.R. Scully,* University of Virginia

Over the past 25 years, investigations concerning the use of continuous and pulsed lasers for surface modification have met with reasonable success in areas of alloying element modification, enhanced surface hardness, structure manipulation, and improvements in corrosion resistance.@footnote 1@ There are several critical attributes of laser surface modification (LSM) that lead to the formation of an amorphous surface, including the ability to promote near-surface compositional uniformity, and due to the use of a pulsed laser (nanoseconds), rapid solidification at quench rates on the order of 10@super 8@ to 10@super 10@ K/s are possible. Moreover, since only the first few micrometers are re-solidified, LSM presents the opportunity to explore the surface amorphization of materials without sacrificing desirable bulk properties such as strength and toughness. This research focuses on the Al-Co-Ce and Fe-Cr-Mo-Er-C-B alloy systems with enhanced glass forming chemistries. In this research, the homogeneity of the starting crystalline ingot has been found to have a major impact on the ability to form an amorphous surface. The LSM surfaces showed several amorphous characteristics in terms of backscattered imaging, diffraction spectra, and corrosion behavior, all of which are signatures of these classes of amorphous materials. Electrochemical analysis of the modified materials showed increased pitting potentials and several characteristics similar to that of fully amorphous, melt spun metallic glass alloy standards. Characterization was performed with scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDXS), Auger electron spectroscopy (AES), conventional and glancing angle X-ray diffraction (XRD), and electrochemical analysis. @FootnoteText@ @footnote 1@ K.G. Watkins, M.A. McMahon, and W.M. Steen, Mat. Sci. and Eng. 231, p. 55 - 61 (1997).

SE-TuP4 Structure and Bonding of V@sub 2@AlC Studied by Theoretical and Experimental Means*, J.M. Schneider, **R. Mertens**, D. Music,* RWTH Aachen, Germany

We have studied V@sub 2@AlC (space group P6@sub 3@/mmc, prototype Cr@sub 2@AlC) by ab initio calculations and used DC magnetron sputtering to synthesize a thin film. The density of states (DOS) of V@sub 2@AlC for antiferromagnetic (AFM), ferromagnetic (FM), and paramagnetic (PM) configurations are also presented. Based on a comparison of the cohesive energies as well as the DOS for the spin polarized structures, we have identified the FM/AFM configuration to be metastable. According to our partial DOS analysis, V@sub 2@AlC can be described as a strongly coupled nanolaminate [Z. Sun, D. Music, R. Ahuja, S. Li, and J. M. Schneider, Phys. Rev. B 70, 092102 (2004)]. Furthermore, we have observed good agreement between the calculated and measured equilibrium volume.

Surface Science
Room Exhibit Hall C&D - Session SS-TuP
Surface Science Poster Session

SS-TuP1 Varying the Interfacial Structure of Alkanethiol Monolayers on Gold Through Controlled Thermal Desorption*, **C.D. Zangmeister**, L.B. Picraux,* National Institute of Standards and Technology

This study investigates the formation of low-density, flat-lying decanethiol chemisorbed on Au prepared by heating the surface covered with a densely-packed, upright monolayer to a surface temperature above the onset of desorption. We determined conditions for preparing the low-density phase of decanethiol by observing the evolution of the surface and interfacial structure as a function of the surface temperature using polarized ultraviolet photoemission spectroscopy. The preparation conditions were similar for single- and polycrystalline gold surfaces. Once the low density decanethiol phase was formed, reflection absorption infrared spectroscopy was utilized to determine the orientation of the carbon chain backbone with respect to the Au surface.

SS-TuP2 Ultrastable Conductance Measurements of Self-Assembled Monolayer Supported Phenylene-Ethylene Oligomers*, **S.U. Nanayakkara**, M.M. Blake, A.A. Dameron, R. Zhang, C. Pochas, M. Kim, P.S. Weiss,* The Pennsylvania State University*; T.P. Pearl,* North Carolina State University*; S. Uppili, D. Allara,* The Pennsylvania State University*; J.M. Tour,* Rice University

We have used alkanethiolate self-assembled monolayers (SAMs) to fabricate support matrices for probing the charge transport properties of both isolated and bundled phenylene-ethylene oligomers (OPEs). By utilizing solution- and vapor-phase manipulation techniques, we can select the distribution of the OPE molecules within the SAM matrix. These fabrication techniques, in combination with the spatial and energy resolution afforded by low temperature scanning tunneling microscopy and spectroscopy, have enabled us to probe the electronic properties of these molecules. We have probed individual substituted OPE molecules in analogous environments to understand the effects of chemical substitution on charge transport. We aim to understand the conductance pathways of these molecules as a function of their chemical structure, physical environment and adsorption site.

SS-TuP3 Geometric and Electronic Structure of Self-Assembled Monolayers on Noble Metal Surfaces: Dodecanethiol on Au, Ag, and Pt*, T.M. Sweeney, J.M. Burst, P.S. Robbert, J.W. Hobson, S.M. Huston, C.A. Ventrice, Jr.,* University of New Orleans*; B. Hayes, **H. Geisler**,* Xavier University

Self-assembled monolayers (SAMs) have been grown by vapor deposition in UHV and by solution growth in ambient conditions on Au(111), Ag(111), Pt(111), and Pt(100) surfaces. The geometric structure of the SAMs has been studied with low energy electron diffraction (LEED), and the electronic structure has been measured with synchrotron-based ultra-violet photoelectron spectroscopy (UPS). The LEED results for Au provide evidence for a lying down, striped phase from 2 L to 40 kL, a disordered, mixed phase up to ~2 ML, and a standing-up, @sr@3x@sr@3 R30° phase beyond ~2 ML of thiol dose. Vapor deposition on Ag results in a disordering of the surface, with a complete loss of the LEED pattern by ~5 kL. Ordered overlayer structures are observed on both the Pt(111) and Pt(100) surfaces at thiol doses below 1 L. For instance, a p(2x2) LEED pattern is observed at 0.1 L which transforms to a @sr@3x@sr@3 R30° pattern at ~.25 L on the Pt(111) surface. Doses beyond ~2 L result in a disordered overlayer on this surface. The UPS spectra for solution growth SAMs on all three substrates are very similar. Four distinct peaks at 6.5, 10, 14, and 20 eV whose intensities are independent of the substrate are observed. The electronic structure of the vapor deposited films depends very strongly on the substrate. Weak thiol peaks are observed for coverages up to 100 kL on Au(111), consistent with the slow uptake observed with LEED. Emission features consistent with a fully saturated SAM are observed on Ag(111) for a dose of ~8 kL. Very weak thiol peaks are observed on the Pt surfaces for coverages up to 100 kL, which indicates that the uptake on Pt is slower than on Au. The ordered overlayer LEED patterns at low coverages, coupled with the very weak thiol features in UPS, point to a dissociative adsorption geometry for vapor deposition on Pt.

SS-TuP4 Comparison of Thiol and Disulfide Based Self-Assembled Monolayers (SAMs) by Reactive Ion Scattering Spectrometry (RISS)*, **K.E. Joyce**,* University of Arizona*; S. Ravindran,* University of Texas*; V.H. Wysocki,* University of Arizona

Reactive Ion Scattering Spectrometry (RISS) was used to investigate self-assembled monolayers (SAMs) formed from symmetric disulfides and thiol solutions of corresponding chain lengths. A series of odd and even alkanethiol (CH@sub 3@(CH@sub 2@)@sub n@SH; n= 15, 16, 17) and disulfide ((CH@sub 3@(CH@sub 2@)@sub n@S)@sub 2@; n= 15, 16, 17) SAMs were probed with benzene and pyrazine projectile ions to investigate both neutralization and reaction differences. RISS utilizes a tandem quadrupole mass spectrometer to select ions of a given mass-to-charge value and collides them with a given collision energy into the surface. Reactions of the ion beam with the surface are sensitive to factors such as the nature of the orientation of the terminal functional group. RISS revealed differences between disulfide and thiol based SAMs in both neutralization characteristics of the films, as evidenced by differences in total scattered ion currents, as well as differences in reactions via hydrogen and methyl abstractions from the surfaces. Systematic studies were conducted where fully formed disulfide based SAMs were introduced to thiol solutions to show incorporation of thiol species. FT-IR and contact angle experiments were also performed to examine SAM film chain-to-chain interactions.

SS-TuP5 The Impact of Molecular Properties on the Geometric Structure of Self Assembled Monolayers of Arenethiols on Cu(111)*, **X. Lin**, K.-Y. Kwon, K.L. Wong, L. Bartels,* University of California at Riverside

Self assembled monolayers (SAMs) of organic molecules on metal surfaces are the subject of great interest due to their utility in nanodevices. The structure of individual SAMs is not only determined by the binding of their constituents to the substrate but also by intermolecular interactions. One challenging problem is to understand how molecule-molecule interactions affect the structure of the monolayer. We explored the impact of these interactions using thiolphenol (TP) molecules on Cu(111) as a model system for aromatic thiol SAMs. Molecular properties can be changed in a systematic fashion by selective substitutions. We have performed STM studies of monolayers of thiolphenol (TP) molecules and several halogen substituted para- and meta-X-TP derivates (where X is Br, Cl or F). For both meta and para substituted molecules we find that the complexity of the monolayers increases with the electronegativity of the substituent, which suggests that electrostatic interactions of the molecular dipole and quadrupole moment play a critical role in determining the film structure. Penta-fluoro-substituted TPs exhibit no ordering at all, while unsubstituted TPs exhibit no long range order, yet are able to form stable aggregates up to seven molecules. Despite the fact that all the studied molecules share the common feature of having a thiol group as linker to the metal substrate, they display a vast diversity in their aggregation behavior as well as in their monolayer structures. This demonstrates the utility of this model system where the molecule-molecule interaction can be finely tuned to exhibit the full spectrum of aggregation behavior, from no ordering via clustering to formation of layers with complex patterns.

SS-TuP6 The Structure and Assembly of Ordered Alkanethiol Monolayers on GaAs (001)*, **C.L. McGuiness**,* The Pennsylvania State University*; D. Blasini,* Cornell University*; S. Uppili,* The Pennsylvania State University*; A. Shaporenko, M. Zharnikov,* University of Heidelberg, Germany*; D. Smilgies,* CHESS*; D. Allara,* The Pennsylvania State University

We demonstrate through glancing angle x-ray diffraction (GIXRD), near edge x-ray adsorption fine structure (NEXAFS), infrared spectroscopy (IRS), x-ray photoelectron spectroscopy (XPS) and contact angle measurements that alkanethiol molecules will form densely packed, translationally ordered monolayers on GaAs(001) by solution adsorption. GIXRD data show that the adlayer molecules form a hcp structure which is incommensurate with the underlying square lattice of the substrate, an indication of extensive reconstruction arising during chemisorption. The combination of IRS and NEXAFS data determine an average molecular axis tilt of 13-15Âº with a high average degree of conformational ordering of the chains. This work gives the first definitive evidence for translationally ordered monolayers on GaAs. The ability to make highly structured and stable molecular films on GaAs will be critical in applications including molecular devices and electron beam resists.

SS-TuP7 Photoelectron Spectroscopy Studies of Potassium Deposition on Self-Assembled Monolayers*, H. Ahn, **J.E. Whitten**,* The University of Massachusetts Lowell

The deposition of potassium in ultrahigh vacuum on alkanethiols self-assembled on gold surfaces has been investigated with X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS). Several issues have been studied, including extent of penetration of the metal and chemical interaction with the organic layer. In the case of methyl-terminated alkanethiols, it is found that potassium penetrates and interacts weakly with the monolayer, as indicated by minimal changes in the valence electronic spectra, even for large metal doses. Angle-resolved XPS and changes in the areas of the K2p, C1s, S2p, and Au4f peaks with increasing potassium dose confirm penetration. Work function measurements, obtained from the widths of the UPS spectra, are consistent with metal diffusion through the methyl-terminated alkanethiols to the gold interface, and work function changes approaching -2 eV are observed for several atomic layers worth of potassium. These types of studies have been performed for a variety of chain lengths and at cryogenic and room temperature. In general it has been found that potassium-induced C1s core level shifts, using XPS when the spectra are referenced to the Fermi level, are a misleading indicator of chemical interaction and essentially disappear when the peaks are referenced to the vacuum level. On the other hand, the Au4f peaks do not shift with respect to the Fermi level. These data suggest that the C1s alkanethiol orbitals are pinned to the vacuum level, and angle-resolved XPS has been to quantify and study this effect as a function of depth.

SS-TuP8 Surface Nitridation of Terphenyl Methane Thiol Self-assembled Monolayer Using N@sub 2@ Neutral Beam Process*, **Y. Ishikawa**,* Tohoku University, Japan*; T. Ishida,* AIST, Japan*; S. Samukawa,* Tohoku University, Japan

To realize the future molecular scale devices, a fine surface modification method is quite important for controlling surface properties of organic molecules, such as the electric properties. Generally, the plasma processes were widely used to modify the surface for not only semiconductor devices but also polymer surface. However, for the surface modification of organic monolayers that can be utilize molecular scale device, the plasma processes cannot be used because of radiation of VUV, UV photons and charged particles from plasma to surface. Namely, the organic monolayers are considered to be broken due to radiation of these particles. To eliminate these radiation damages, we have already proposed the neutral beam process.@footnote 1,2@ This process could perfectly prevent the charged particles and ultraviolet photons to the surface and only the low energy neutral beam (accelerated atom and molecular beam) were irradiated to the substrates. In this paper, the pulse-time-modulated (TM) N@sub 2@ beam irradiation@footnote 1@ was investigated to control the surface nitridation of terphenyl methane thiol self-assembled monolayer (TP1-SAM).@footnote 3,4@ The N@sub 2@ neutral beam irradiation was modulated at a few tens microseconds to control the degree of surface nitridation. By using the novel modification method, we investigated the surface nitridation of TP1-SAM with maintaining the bulk structure. After the beam irradiation, we evaluated the amount of surface nitridation using the x-ray photoelectron spectroscopy. We found that the TM N@sub 2@ beam could precisely control the surface nitridation of TP1-SAM by changing the beam modulation period. @FootnoteText@ @footnote 1@ S. Samukawa et al.: J. Vac. Sci. Tech., A22, 245 (2004)@footnote 2@ Y. Ishikawa et al.: AVS 51st international symposium, PS+BI-FrM9 (2004)@footnote 3@ T. Ishida et al.: Langmuir, 18, 83 (2002)@footnote 4@ T. Ishida et. al., Langmuir, 18, 10499 (2002).

SS-TuP10 Reaction Site Selectivity of Analyte Gases on Metallophthalocyanines: A Density Functional Theory Study*, **N.L. Tran**, S.R. Bishop, G.C. Poon, A.C. Kummel,* University of California at San Diego

Numerous studies have reported the use of metallophthalocyanines (MPcs) as thin film sensors for analyte gases, but a basic understanding of gas chemisorption onto these metal coordination complexes is lacking. Density functional theory was used to investigate the mechanism of chemisorption of two different analytes, NO and NH@sub 3@, onto two different MPcs, CoPc and FePc. Four analyte binding sites on the MPcs were investigated: (i) metal centers, (ii) inner ring nitrogen atoms, (iii) outer ring nitrogen atoms, and (iv) organic rings. For NO on FePc and CoPc, simulations show chemisorption onto the metal centers and physisorption onto the outer ring nitrogens and organic rings. In contrast, NH@sub 3@ chemisorbs onto the FePc metal center and physisorbs onto the Co metal. All other binding sites were not energetically favorable. Additionally, these calculations show a multi-step absorption mechanism in which NO initially binds to the inner ring nitrogens and then undergoes a barrierless migration to the deep chemisorption well on the metal centers for FePc and CoPc. PDOS simulations reveal that the binding of NO and NH@sub 3@ to the FePc metal center significantly alters the electronic structure of the clean FePc. However the two systems have opposite charge transfer mechanisms: charge is accepted by the NO chemisorbate from the Iron metal but is donated from the NH@sub 3@ chemisorbate to the Iron metal. These different charge transfer mechanisms will differentially affect charge relaxation times and the photoconductivity threshold in an MPc film and therefore can be used to identify analytes instead of just measuring analyte concentration. Additionally, simulations are being performed to study the possibility of subsurface diffusion of the NO molecule into the bulk.

SS-TuP11 Thermochromism Effects in Poly(3-hexylthiophene)*, **D.Q. Feng,*** University of Nebraska-Lincoln*; P.A. Dowben,* University of Nebraska-Lincoln, US

We find evidence for a gradual semiconductor to insulator transition in poly(3-hexylthiophene), that appears to be mediated by a low density of defects states within the highest occupied molecular orbital to lowest unoccupied molecular orbital gap. The photoemission and transport measurements indicate that a loss of charge mobility occurs with decreasing temperature, while the molecular configuration also changes with temperature. Defects states have been identified in photoemission and these defects states are believed to be very heterogeneous.

SS-TuP12 Adsorption and Decomposition of Triethylsilane on Si(100)*, J. Lozano, D. Early, L. Bockewitz, **J.H. Craig, Jr.**, P.W. Wang, K.R. Kimberlin,* Bradley University

The adsorption and decomposition of triethylsilane (TES) on Si(100) were studied using temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS), and x-ray photoelectron spectroscopy (XPS). Si(100) samples were dosed with TES at 100K. Desorption of mass 27 (attributed to ethylene) takes place at 750K, followed by desorption of hydrogen at 815K. This is indicative of a ???-hydride elimination process that results in at least partial removal of carbon species from the surface. At multilayer coverages, physisorbed species accumulate on the surface, as indicated by a low temperature desorption peak at 170K. At the highest TES exposures (~10L), a second low temperature TPD peak appears at 280K. This suggests that the second-layer physisorbed state is slightly more tightly bound than multilayer TES. In order to confirm this, HREELS and XPS data were obtained immediately following sequential thermal anneals to increasing temperatures, which were determined by landmark features in the TPD spectra. A model of the thermal evolution of TES on Si(100) based on the results obtained will be presented.

SS-TuP13 Low Temperature Decomposition of Triethylsilane on Si(100) by Electron Irradiation*, **J. Lozano**, D. Early, L. Bockewitz, P. Petrany, J.H. Craig, Jr., P.W. Wang, K.R. Kimberlin,* Bradley University

Electron-induced decomposition of triethylsilane (TES) on Si(100) at 100K was studied using temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS), electron stimulated desorption (ESD), and x-ray photoelectron spectroscopy (XPS). Si(100) samples were dosed with TES and then irradiated with 600-eV electrons for 5 minutes. During electron irradiation, ESD of neutral particles was monitored. Only a small hydrogen ESD signal was detected at all TES coverages. Following electron irradiation of multilayer TES/Si(100), TPD data exhibited decreased desorption of physisorbed species and a dramatic increase in mass 2, 27, and 59 desorption, compared to TPD from un-irradiated surfaces. This indicates that electron irradiation resulted in decomposition of TES and deposition of large fragments on the surface. Fragmentation of TES by electron irradiation was studied by obtaining HREELS and XPS data following sequential thermal anneals of the electron-irradiated surface to increasing temperatures.

SS-TuP14 Molecular View of the Selforganization Processes on Silicon: Experimental and Computational Studies of Nitrobenzene and Hexafluoroacetylacetone on Si(100)-2x1*, **L.P. Méndez De Leo**, L. Pirolli, A.V. Teplyakov,* University of Delaware

Molecular selforganization on semiconductor surfaces bears a variety of future applications: from deposition processes to molecular electronics. Here we present two different reactions on Si(100)-2x1 surface studied by an array of surface analytical techniques and by computational methods. The reaction of nitrobenzene on Si(100) surface is a prototypical model reaction for understanding the interaction of bifunctional molecules with the surface and for directing self-organization processes at cryogenic temperatures. The preferred reaction of the nitro-group has been studied previously and, along with the exceptional thermal stability of the resulting monolayer, provides an opportunity to manipulate surface reactions that have a long list of possible pathways. Computational analysis together with the vibrational studies suggest that only a few types of surface bonding are possible in this reaction and the interaction between the neighboring chemisorbed nitrobenzenes lay a groundwork for studies of electron transfer processes involving the @pi@-@pi@ interaction of the phenyl groups. Hexafluoroacetylacetone (hfac) is a common ligand in chemical vapor deposition processes of copper. The interaction of this ligand with the Si(100)-2x1 surface is of paramount importance for the deposition processes, at the same time, it possesses several functionalities and the utilization of the preferential binding of these functional groups to the surface can be used in the future not only to modify the interactions of the organometallic precursors with the substrate but also to understand the general rules in functionalization of the surface with complex multifunctional molecules. Just like in the case of nitrobenzene, computational methods were used in conjunction with the experimental studies to elucidate the mechanism of hfac interaction with Si(100)-2x1.

SS-TuP16 Adsorption and Dissociation Studies of Tri-ethylgermane on the Si(100) Surface*, **A. Brickman**, P. Petrany, J. Lozano, J.H. Craig, Jr., P.W. Wang,* Bradley University

Adsorption of tri-ethylgermane (TEG) on the Si(100) surface has been studied using temperature programmed desorption (TPD), electron stimulated desorption (ESD) in a time-of-flight mode, and high resolution energy loss spectroscopy (HREELS). Evidence for a beta-hydrogen elimination process will be presented in desorption spectra. Electron driven dissociation effects on the adsorbed TEG layer will be presented. The extent to which germanium is deposited on the Si(100) surface subsequent to TEG dissociation will also be discussed as characterized by X-ray photoelectron spectroscopy (XPS).

SS-TuP17 The Adsorption Structure of Histidine on Ge(100)*, **S.J. Jung**, S. Kim,* Korea Advanced Institute of Science and Technology (KAIST), Korea*; S. Hong,* Sejong University, Korea

The adsorption of histidine molecule on the Ge(100)-2×1 surface was investigated using both scanning tunneling microscopy (STM) and the density functional calculation. Various adsorption features of histidine are founded to be formed under different conditions of temperatures and coverages. When histidine is exposed to a clean Ge(100) surface at 300 K, the histidine appears as round shaped bright protrusion in STM image, which is randomly distributed over the surface. After annealing the surface at 380 K, we found a short range ordering in molecular rows. When histidine is deposited onto Ge (100) at 380 K, histidine is found to form dumbbell shape protrusions that are located in either parallel or vertical direction to the dimer row. At the saturation coverage (Θ= 0.25 ML), however, the STM image show globally ordered array consisted of dumbbell shape features without regard to the direction of dimer row of the Ge (100) surface. Such global ordering implies that the interaction between histidine molecules is much more significant than the interaction between the molecules and the surface dimer. The ab initio calculation also suggests that the surface at saturation coverage has an additional stability, induced by the lateral interaction, compared to that at low coverage. Based on the STM results and ab initio calculation, we will present the adsorption structures, inter-molecular interaction and ordering of histidine molecules on the Ge(100) surface.

SS-TuP18 Chiral Attachment of Styrene Mediated by Surface Dimers on Ge(100)*, **Y.J. Hwang,*** Korea Advanced Institute of Science and Technology (KAIST), South Korea*; A. Kim,* Korea Advanced Institute of Science and Technology (KAIST), South Korea, Korea*; E.K. Hwang, S. Kim,* Korea Advanced Institute of Science and Technology (KAIST), South Korea

We determine the absolute chirality of adsorbed styrene using scanning tunneling microscope (STM) and demonstrate a novel method for the achiral molecule to produce dimeric enantiomers and diastereomers covalently bonded to the Ge(100) surface. On the Ge(100) surface, styrene adsorbs in a paired end-bridge between two neighboring Ge dimers within the same dimer row (PEB) as well as on the top of a single Ge-Ge dimer (OT). The OT configuration is classified into (S) and (R) OT chiral products according to the direction in which styrene molecule attacks the Ge dimer. Similarly, in case of paired adsorption, we found enantiomeric (R,R)- and (S,S)-trans-PEB and diastereomeric (R,S)-cis-PEB configurations through

STM images.@footnote 1@ Temperature programmed desorption (TPD) spectra indicated that the desorption temperatures for the OT and PEB configurations are 320 K and 365 K, respectively. STM measurements indicate that the OT configurations is converted into the thermodynamically more stable PEB configurations either by annealing a styrene-adsrobed Ge surface at 340 K or by scanning the Ge surface at high bias voltages. Such conversion of chiral configurations suggests the possibility of the controlled adsorption of chiral molecules on the surface. Therefore, we anticipate that the chiral structures prepared by paired adsorption will provide chiral organic hybrid systems on semiconductor surfaces for potential application to semiconductor-based molecular devices, chiral sensors, and heterogeneous enantioselective catalysis. @FootnoteText@@footnote 1@ Hwang, Y. J.; Kim, A.; Hwang, E.; Kim, S. J. AM. CHEM. SOC. 2005, 127, 5016-5017

SS-TuP19 Phonon-Activated Electron-Stimulated Desorption of Halogens from Si(100)-(2x1)*, **B.R. Trenhaile**, V.N. Antonov, G.J. Xu, A. Agrawal, A.W. Signor, R.E. Butera, K.S. Nakayama, J.H. Weaver,* University of Illinois at Urbana-Champaign

Spontaneous desorption of Cl, Br, and I from n- and p-type Si(100)-(2x1) was studied with scanning tunneling microscopy at temperatures of 620 â?" 825 K where conventional thermal bond breaking should be negligible. The activation energies and prefactors determined from Arrhenius plots indicate a novel reaction pathway that is initiated by the capture of electrons that have been excited by phonon processes into Si-halogen antibonding states. This configuration is on a repulsive potential energy surface, and it is sufficiently long-lived that desorption occurs, as in electron-stimulated-desorption. Surprisingly, the desorption rates for differently doped samples crossed and, above a critical temperature, the reaction with the largest activation energy had the highest rate. This is explained by large entropy changes associated with the multiphonon nature of the electronic excitation. For Cl desorption from p-type Si, these entropy changes amounted to 34 kB. They were 19 kB, 13 kB, and 8 kB for Br desorption from p-type, lightly-doped n-type, and heavily-doped n-type Si, respectively. The desorption rates for I were nearly three orders of magnitude larger than the rates observed for Cl and Br. Here, the Si-I antibonding states overlap the conduction band minimum, and we propose that electrons impinging on the surface with this energy can be captured by the Si-I antibonding states. Together, these results reveal that a complex relationship exists between phonons and electronic excitations during chemical reactions at surfaces.

SS-TuP20 Water Etching of Hydrogen-Terminated Si(100): Implications for Oxidation*, **S.K. Green**,* Smith College*; M.F. Faggin, M.A. Hines,* Cornell University*; K.T. Queeney,* Smith College

While it has been known for some time that deoxygenated H@sub 2@O will etch hydrogen-terminated Si(100), our recent work shows that this etching generates a surface of surprising homogeneity. Transmission infrared spectroscopy is used both to examine the mechanism of this etching process and to decipher the surface termination of the structures formed. Analysis of both the stretching and bending modes of SiH@sub x@ species reveals characteristic {100} and {111} facets that can be related to structures formed on extended (100) and (111) surfaces. Selective isotopic labeling reveals that the initial, H-terminated surface is completely removed within 10 minutes' immersion in room-temperature, deoxygenated H@sub 2@O. The rate of this reaction is therefore fast compared to the rate of oxidation of H:Si(100) by O@sub 2(aq)@ that is normally present in air-equilibrated H@sub 2@O, making the etching process a critical factor in the oxidation of Si(100) in neutral or basic aqueous solutions.

SS-TuP21 Substrate-Bias-Dependent Orientation-Selective-Epitaxial Growth of CeO@sub 2@ Thin Films on Si(100) Substrates by Magnetron Reactive Sputtering*, **T. Inoue**,* Iwaki Meisei University, Japan*; D. Kukuruznyak, T. Chikyo,* National Institute for Materials Science, Japan*; K. Kato,* Fukushima Technology Centre, Japan

Although many reports have been made on the growth of CeO@sub2@(110)/Si(100), orientation selective epitaxial (OSE) growth of CeO@sub 2@(100) and CeO@sub 2@(110) layers is found to be capable by controlling substrate bias and plasma power in reactive dc magnetron sputtering enhanced with an inductively coupled rf plasma.@footnote 1@ We adopted two step growth method; ultrathin metallic Ce layer deposition at room temperature using Ce metal target followed by silicidation process at several hundreds degree C, and subsequent reactive sputtering in an Ar/O@sub 2@ mixture environment at elevated temperature. Reactive magnetron sputtering is performed at rf power of 50 W for induction coil and 120 W for cathode dc plasma power under substrate bias ranging between -25 and +25 V varied by 5~V step. Growth rate is controlled in between 0.2 and 0.4 nm/s varying Ar gas flow between 4 and 15 sccm. Oxygen gas flow for reactive sputtering is 1 sccm. CeO@sub2@(100) layers grow under substrate bias around both +15 and -15 V with a width of approximately 10 V, otherwise CeO@sub2@(110) layers grow. The orientation selection is found to be also dependent on plasma power, in other words the growth rate: upper limit in growth rate exists for (100) layer growth, above which (110) layer grow. Precise mapping of growth parameters for OSE, in terms of substrate bias and growth rate, for the growth of CeO@sub 2@(100) films are attained from a lot of growth experiments. In order to get insight into orientation selectivity depending on substrate bias, we are making systematic experiments to study orientation component changes with substrate bias in CeO@sub 2@ layers, which leads to a clue for understanding the relation between orientation of nuclei and substrate bias. We also demonstrate the experimental results indicating effectiveness of assistance by oxygen radical beams on reactive sputtering; successful epitaxial temperature lowering and crystalline quality improvements. Characterization of the epitaxial films are carried out using RHEED, XRD, XTEM and AFM. This orientation selective epitaxial growth (OSE) technology will be useful for sophisticated structure using multiple layer epitaxy. @FootnoteText@ @footnote 1@ T. Inoue et al., J. Vac. Sci. Tehcnol. A 22(1), 46 (2004).

SS-TuP22 Measurement of Surface States Above the Valence Band Maximum in n-type GaN(0001) Using Angle-Resolved Photoemission Spectroscopy*, **L. Plucinski**, L. Colakerol, S. Bernardis, Y. Zhang, K.E. Smith, I. Friel, T.D. Moustakas,* Boston University

We have performed a high resolution angle-resolved photoemission study of N-polar GaN(000-1).@footnote 1@ We have observed sharp dispersive surface states extending approximately 2 eV above the valence band maximum (VBM). These states agree with those predicted for a N-polar Ga-adlayer GaN(000-1) 1x1 reconstructed surface. Samples were grown by plasma-assisted molecular beam epitaxy on c-plane sapphire. They were doped with Si and the free-carrier concentration was 3 x 10@super 18@ cm @super -3@ which resulted in a slightly degenerate n-type material at room temperature. Experiments were performed at the U5UA undulator beamline at the NSLS, using a Scienta SES100 electron energy analyzer. Clean surfaces were prepared in situ by sputtering with nitrogen ions and annealing in UHV. Samples were held at 120 K when recording spectra. We have found a full width at half maximum for the surface state feature of 400 meV at K-point of surface Brillouin zone. The width is limited by surface imperfections and the existence of reconstructions on the surface other than a simple 1x1. Our results are similar to those obtained for p-type GaN.@footnote 2@ However, in case of p-type GaN the surface likely contained 30 degree rotated domains.@footnote 3@ We show that in the case of n-type GaN the surface is free of domains. @FootnoteText@ @footnote 1@ Supported in part by the NSF DMR-0311792, by U.S. ARO 40126-PH, and by U.S. AFOSR. Our spectrometer system is funded by U.S. ARO DAAD19-01-1-0364. Experiments performed at the NSLS which is supported by the U.S. DOE, Divisions of Materials and Chemical Sciences.@footnote 2@ P. Ryan, Y. C. Chao, J. Downes, C. McGuinness, K. E. Smith, A. V. Sampath, and T. D. Moustakas, Surf. Sci. 467, L827 (2000).@footnote 3@ F.-H. Wang, P. Krueger, and J. Pollmann, Surf. Sci. 499, 193 (2002).

SS-TuP23 Step Edge Diffusion in Strained Compound Semiconductors*, **C. Pearson**,* University of Michigan-Flint*; J. Mirecki Millunchick,* University of Michigan

Understanding the growth of strained alloys films is an enduring problem in surface science. Models of strained film growth based on elastic strain energy predict unique morphologies for different strain: islands upon large terraces for compressive films and mesas separated by trenches for tensile films. Using a combined MBE-STM system, we have imaged 2 ML thick films both in compression (InAs or GaSb) and in tension (GaAs or AlAs) grown on InP(001) near T=480°C using a group III growth rate of ~0.2 ML/s with an approximate group V/III ratio of 5. A roughness analysis reveals that the skewness of the height distribution for InAs is positive, which is indicative of a morphology dominated by islands while for AlAs the skewness is negative, which is indicative of a morphology dominated by holes. These results agree with the previously described morphologies predicted using elastic strain energy considerations. The Ga containing compounds also follow this strain energy trend, except the terraces or mesas have significantly rougher steps and higher surface anisotropies. These observations suggest that in addition to the sign of the misfit strain, factors such as step edge diffusion contribute to surface roughness. From an analysis of the images we compute the step edge density (step edge length per unit area) versus deposition flux and use a recent level set model@footnote 1@ to extract values of step edge diffusion. These results may explain the variety of microstructures observed in short period superlattice structures of these compounds that exhibit lateral composition modulation. @FootnoteText@ @footnote 1@ C. Ratsch, J. Garcia, and R. E. Caflisch, submitted to Applied Physics Letters.

SS-TuP24 Comparative Study of the Initial Oxidation Kinetics on Si(001) and Ti(0001) Surfaces by Real-Time Ultraviolet Photoelectron Spectroscopy*, **Y. Takakuwa**, S. Ogawa, M. Ohira,* IMRAM, Tohoku University, Japan*; Y. Mizuno,* Stanford University

Oxidation on Si and Ti surfaces leads to growth of SiO@sub 2@ and TiO@sub 2@ layer, respectively. In order to clarify the behavior of adsorbed oxygen during growth of oxide, the initial oxidation kinetics on Si(001)2x1 and Ti(0001)1x1 surfaces was comparatively investigated by real-time ultraviolet photoelectron spectroscopy to measure the oxygen uptake and work function @phi@ simultaneously. Onn the Si surface at 357°C, the @phi@ increases gradually with increase of O@sub 2@ dosage after showing a dip due to negative changes, while the dip disappears with elevating temperature. The negative change of @phi@ means diffusion of adsorbed oxygen into the subsurface. On the other hand, a dip in @phi@ appears at temperatures above 300°C on the Ti surface. This suggests that adsorbed oxygen on the Ti surface can easily diffuse into the subsurface when elevating temperature, although such diffusion of adsorbed oxygen tends to occur on the Si surface when lowering temperature. The difference of adsorbed oxygen behavior between Si and Ti surfaces is discussed in terms of the O@sub 2@ dissociative adsorption kinetics and crystallographic nature of oxide, amorphous SiO@sub 2@ and crystalline TiO@sub 2@.

SS-TuP25 Stress-induced Transformation between Si(5 5 12)-2x1 and Si(7 7 17)-2x1*, S. Cho, **J.M. Seo,*** Chonbuk National University, Korea

From the reconstructed Si(5 5 12)-2x1, the area of locally-converted Si(7 7 17)-2x1 has been detected by scanning tunneling microscopy(STM). The atomic structure of Si(7 7 17)-2x1 has turned out to be the same as that of Si(5 5 12)-2x1 with missing one of (337) sections, namely D(337) with a dimer-facing-adatom(D/A) row. In this structural transformation from (5 5 12) to (7 7 17), neither the number of atoms nor the dangling-bond number changes, but the surface atoms simply rebond under the external stress originating from the (113) facet parallel to 1-D row. By the distribution of (7 7 17) domain, the direction and size of compressive surface-stress on Si(5 5 12)-2x1 can be deduced, implying that (7 7 17) can be utilized as a stress-indicator of nanometer scale on (5 5 12).

SS-TuP26 Thermal Stability of Nikel Silicide Layer on Si, Relaxed-SiGe/Si, Strained-Si/relaxed-SiGe/Si Heterostructure*, **J.H. Ko**, C.H. Jang,* Sungkyunkwan University, Korea*; S.H. Kim, Y.-J. Song,* Electronics and Telecommunications Research Institute, Korea*; N.-E. Lee,* Sungkyunkwan University, Korea

MOSFET device utilizing a strained-Si channel on relaxed SiGe buffer layer is one of the most promising structure for the next-generation CMOS integration scheme below 50 nm technology node because of its high channel mobilities compared to bulk Si and compatibility with conventional Si CMOS processes. Rapid thermal annealing was performed at 400 °C and then post thermal annealing was performed at of 600~800 °C as following process. Nickel silicide was formed on strained-Si/relaxed-SiGe/Si (001) and relaxed-SiGe/Si (001) and Si (001) using a sacrificial strained-Si layer and its morphological characteristics were investigated. Nickel silicide layers were grown by rapid thermal annealing of the samples with the structure of Ni (10.92 nm)/strained-Si (20 nm)/relaxed-SiGe/Si (001) at the annealing temperature (TA) range of 400~800 °C. And we deposited Ni at each 11nm and 21nm to know what is different. When we deposited 11nm Ni that it's interface roughness very bad but 21nm Ni deposited whose interface roughness improved. The phase formation, surface and interfacial morphologies, and electrical properties of the resulting sample were characterized by various measurement technique, including X-ray diffraction, scanning electron microscopy, cross-sectional transmission electron microscopy and the four-point probe method. As the result when we measured sheet resistance Ni 11 nm on strained-Si/relaxed-SiGe/Si (001) and relaxed-SiGe/Si (001) and Si (001) it were determined to be 9.778, 11.083, 8.464 @ohm@/sq. at 400 °C and it were determined 4.428, 5.453, 4.715 @ohm@/sq. at 400 °C 21 nm. Sheet resistance were determined 160.98, 78.79, 138.633 and 92.397, 65.857, 146.875 @ohm@/sq. at 800 °C 11nm and 800 °C 21 nm, respectively

SS-TuP27 Lithium Hydride and Lithium Amide for Hydrogen Storage*, **J. Engbaek**,* Technical University of Denmark, Denmark*; G. Nielsen,* Technical University of Denmark*; I. Chorkendorff,* Technical University of Denmark, Denmark

Hydrogen storage is a serious showstopper for using hydrogen in the transport sector therefore this field has gained renewed interest. Lithium amid has a high hydrogen storage capability; 10.4wt.% hydrogen. In this study surface reactions of thin films of lithium with hydrogen and ammonia is studied under well controlled conditions with pure hydrogen and ammonia in a UHV-chamber. Thin well-characterized Lithium films from sub monolayer to several monolayers were grown on a nickel(111). The films of pure lithium and films reacted with hydrogen and ammonia were characterized with Auger, TPD and LEED. From the LEED patterns we have found that one monolayer of pure lithium form a stable 4x4 reconstructed surface with a coverage of 3 Li atoms to 4 Ni atoms. Lithium hydride was made by exposing a pure lithium film utilizing an atomic hydrogen source. TPD experiments were used to investigate the stability of the lithium / lithium hydride films and surprisingly we have found that lithium evaporate before lithium hydride. Similarly the stability of the lithium hydride / lithium amid was investigated by evaporating Lithium in an atmosphere of ammonia to make thin films of lithium amid. TPD experiments showed that lithium amid decompose at an even higher temperature than lithium hydride and lithium. This significantly complicates the use of lithium amid powder as a hydrogen storage system. The results made under UHV are compared to experiments on ball milled lithium hydride and lithium amid powders.

SS-TuP28 Photoemission and Secondary Ion Mass Spectrometry Study of Uranium Passivation by Ion Implantation*, **A.J. Nelson**, T.E. Felter, K.J. Wu, C. Evans, J.L. Ferreira, W.J. Siekhaus, W. McLean,* Lawrence Livermore National Laboratory

Implantation of C@super+@ ions into U@super238@ produces a physically and chemically modified surface layer that prevents further air oxidation and corrosion. X-ray photoelectron spectroscopy and secondary ion mass spectrometry were used to investigate the surface chemistry and electronic structure of this C@super+@ ion implanted polycrystalline uranium compared to an unimplanted region of the sample, both regions exposed to air for more than a year. In addition, scanning electron microscopy was used to examine and compare the surface morphology of the two regions. High-resolution U 4f, O 1s and C 1s core-level and valence band spectra clearly indicate carbide formation in the modified surface layer. The time-of-flight secondary ion mass spectrometry depth profiling results reveal an approximately 200 nm thick UC layer with little or no residual oxidation at the carbide layer/U metal interface and a small amount of oxidation at the surface. This work was performed under the auspices of the U.S. Dept. of Energy by the University of California Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

SS-TuP29 Surface Chemistry at a LiF-BeF Molten Salt / Beryllium Metal Interface: Probing the Structure and Composition of the Post-Reaction Interface with Microscopy and Electron Spectroscopy*, P.J. Pinhero, **G.R. Smolik**, M.F. Simpson, R.A. Anderl, J.P. Sharpe, D.A. Petti,* Idaho National Laboratory

Molten FLiBe (2LiF:BeF2) is a candidate as a cooling and tritium breeding media for future fusion power plants. Neutron interactions with this salt will produce tritium and excess free fluorine ions. Beryllium metal has been demonstrated as an effective REDOX control agent to prevent the free fluorine from reacting with structural metal components. Simply-designed experiments were performed to measure the extent and rate of Be solubility in a FLiBe mixture that was continuously supplied with HF. This paper presents results from post-test examination of the reacted surfaces. This information provides a good link to understanding the reactions taking place at the interface between the molten salt solution and the Be rod. Potential influences of bi-metal exposures, some with direct coupling, e.g., Be to Ni and Be to Fe were examined. The impacts of the bi-metal contacts upon Be dissolution in the FLiBe and potential alloying with the transition metals are examined using scanning electron microscopy (SEM), atomic force microscopy (AFM), scanning Auger microscopy (SAM), and x-ray photoelectron spectroscopy (XPS).

SS-TuP30 Tuneable Rough Surfaces: A New Approach for Elaboration of Superhydrophobic Films*, **L.M. Lacroix**, M. Lejeune, L. Ceriotti, M. Kormunda, T. Meziani, P. Colpo, F. Rossi,* Joint Research Centre Ispra, European Commission, Italy

The hydrophobic and repelling solid surfaces have found a large utility on our daily lives. The present work describes the process enabling the production of superhydrophobic surfaces by tailoring their surface topography and chemical properties. These surfaces have been developed using a simple plasma based techniques combining plasma etching and plasma polymerization on silicon substrates. These techniques have been chosen because they provide features such as large area processing and high reproducibility. The key step of this process is the modification of the surface topography of the substrate to create high roughness before deposition of fluorocarbon coating. The roughness on silicon wafer is induced by the over-etching of a photoresist layer by a SF6 plasma treatment. The different layers obtained exhibit contact angles from 102 up to 180 depending of the preparation conditions. The observations of the topology by scanning electron microscopy reveal that the presence of dendrites on the surface of the substrate favors the superhydrophobicity of the films. The variations of the contact angle have been explained using the Wenzel's or Cassie's models.

SS-TuP31 Friction Force Microscopy on Monolayer NaCl Films*, P. Delage, T. Filleter, S. Maier,* ***R. Bennewitz,*** McGill University, Canada

Friction and wear on metal surface can be greatly reduced by solid lubricant layers. We have performed Friction Force Microscopy on a model system, ultra-thin films of NaCl on a Cu(100) substrate, in order to study the microscopic mechanisms of friction in solid lubricant films. The NaCl films were grown by means of molecular evaporation in ultra-high vacuum conditions. Large islands of monolayer films are covered with nanometer-scale rectangular islands forming the subsequent layers. The decay of island density close to the edge of the film suggests a low barrier for NaCl molecules diffusing from the first monolayer to the copper substrate. In regions where the film grows over substrate terraces, islands density increases while islands size decreases. Stable friction experiments were possible even on single monolayers of NaCl, and atomic stick-slip processes have been recorded.

SS-TuP32 Single Asperity Atomic Force Microscope Studies of the Chemical Mechanical Planarization of Silicate Glasses@footnote 1@*,* ***F. Stevens****, S.C. Langford, J.T. Dickinson,* Washington State University

The Atomic Force Microscope (AFM) is not only an imaging tool, but also can be employed to apply highly localized stresses to a surface. In the presence of liquids, we can investigate a number of tribochemical processes. Here we present the results of fundamental studies of the simultaneous application of chemical agents and mechanical stress to amorphous sodium trisilicate. We show the consequences of combining highly localized mechanical stress (due to contact with the AFM tip) with exposure to aqueous solutions of known pH. This experiment incorporates many features of single-particle/substrate/slurry interactions in Chemical Mechanical Planarization (CMP). Importantly, we show quantitative, correlated data on the wear of both the AFM tip and the glass substrate. The significant modification of the tip during a single wear experiment has profound effects on the rate of material removal from the exposed surface. Such measurements allow us to determine how substrate wear depends on the stress applied by the tip. In addition, the temperature of the solution and substrate can be changed over a limited range. We examine solid surfaces of silicate glasses, inorganic single crystals, and silicon nitride. Quantitative models are presented to account for the observed nanometer-scale surface modification. @FootnoteText@ @footnote 1@This work was supported by the National Science Foundation.

SS-TuP33 Non Contact Polishing Technique for Metal Foils*,* ***C.C. Chang,*** Industrial Technology Research Institute, Taiwan, R.O.C., Taiwan*; C.J. Wu,* Industrial Technology Research Institute, Taiwan, R.O.C.

Non-contact polishing technique for surface treatment of metal foils has been studied. This paper presents a successful electropolishing technique to deal with the surface of stainless steel foils. This technique is capable of polishing large area(over 200mm width),ultra thin(below 50µm thick) metal foils to be with electric grade surface(Ra<0.02µm), and potential for mass production. The metal foils with electric grade surface could be used of a substrate of flexible electronic devices.

Vacuum Technology
Room Exhibit Hall C&D - Session VT-TuP
Vacuum Technology Poster Session

VT-TuP1 Vacuum Measurement by Carbon Nanotube Field Emission*,* ***I.M. Choi****, S.Y. Woo,* KRISS (Korea Research Institute of Standards and Science), Korea

A new vacuum measurement technology using carbon nanotube(CNT) field emission effect has been designed and manufactured. The fabricated pressure sensor is a triode type similar with a conventional ionization gauge, but has planar structure similar with a Field Emission Display. Due to the excellent field emission characteristics of CNT, it is possible to make a cost effective cold cathode type ion gauge. The triode type CNT sensors have been manufactured by screen-printing method and by thermal CVD growth method. The glass grid with Cr deposited by E-Beam put on the cathode with the gap of 200 mm between two electrodes was manufactured. By the voltage applied to the grid, the electrons emitted from the carbon nanotubes ionize gas molecules in the chamber and the ionized molecules are gathered to the collector. On this occasion, two modes are available to detect the gas density in the chamber; one is electron emission mode, the other is ionization mode. In the electron emission mode, the collector voltage is controlled a little higher than the grid voltage. On the other hand, the collector voltages are controlled lower than the grid voltage to obtain a large ionization ratio in the ionization mode. The current ratio shows increase characteristic according to the pressure in each mode. The ionization characteristics are dependent on the gas and the voltage applied to the grid and the collector. In this paper, the various metrological characteristics of the home made pressure sensor utilizing carbon nanotubes will be shown.

VT-TuP2 Monte Carlo Simulation of Transmission Probability of Gas on Thin Orifice Considering Specular Reflection*,* ***M. Shiro,*** National Institute of Advanced Industrial Science and Technology (AIST), Japan*; M. Hirata, H. Akimichi,* AIST, Japan

To estimate the conductance of an orifice, the influence of its thickness on the transmission probability of gas molecules should be considered. In general, the probability is calculated assuming that molecules hitting inner wall of the orifice reflect with cosine law. However, a specular reflection of gas molecules on the wall should be also considered on the calculation judging from that the accommodation coefficient of a spinning rotor gauge depends on gas species. In such case, it is difficult to calculate the probability analytically. In this study, the probability considering the specular reflection was calculated by the Monte Carlo simulation. The results are as follows, 1) the probability increases with the ratio of the specular reflection. 2) This increment is significant in thick orifice. Even if the thickness is small, it is necessary to consider the effect of the specular reflection. If the specular reflection elements are1%, 3% and 10%, this effect increases the probability 0.1% by the increase of the ratio L/r of thickness L to radius r of the orifice greater than 0.2, 0.07 and 0.02, respectively. In case of thin orifice, the probability can be expressed in a simple equation of the L/r and the ratio of specular reflection. The great portion of molecules passes through the orifice directly. Molecules reflecting in specular on the inner wall of the orifice pass through the orifice. 50% of remaining molecules hitting the wall also pass through the orifice. The deviation of this equation from the result of the simulation is less than 0.1% in the range of L/r<0.2, even if 10% of gas molecules reflected in specular.

VT-TuP4 Selection of State Variables for Diagnosing Dry Vacuum Pumps*,* ***J.Y. Lim****, W.S. Cheung,* Korea Research Institute of Standards and Science*; K.-H. Chung,* Korea Research Institute of Standards and Science, Korea

Detection of degradation and failure-related symptoms of dry vacuum pumps has been currently hot-issued in the semi-conductor and display process lines since the loss time and costs due to abnormal malfunction are astronomically rising. The baseline for the detection is direct monitoring of all state variables from target pumps such as currents, exhaust pressure, vibration, sound pressure, purge gas, temperature, etc. However, the analyzed results show that the state variables are very closely correlated each other, and their factorization may be required for the symptom detection. Also, confusion for the selection has been frequently arisen since vacuum pumps of the same type and of about the same size offered by different manufacturers frequently have minor or even large differences in their mechanical structures. To achieve the process and pump state monitoring ability, gas-type independent vacuum gauges have been installed at the very near pump inlet to monitor the inlet pressure variation with respect to the process time. Five 600 m3/h dry vacuum pumps of the same type have been selected, and tested in the laboratory as well as the actual process line for analyzing state variables. The resultant variability coefficient of the inlet pressure was less than 3.5% above 0.05 mbar corresponding to the actual process pressure range. In the case of the power consumption, the coefficient was above 10%. This very meaningful information provides us with the inlet pressure as the most significant state variable for the detection of degradation and failure-related symptom in the pump type or size independent manner.

VT-TuP5 Active Algorithms for State-Variable Monitoring of Dry Vacuum Pumps*, **W.S. Cheung**, J.Y. Lim, C.U. Cheong,* Korea Research Institute of Standards and Science*; K.-H. Chung,* Korea Research Institute of Standards and Science, Korea

Demands on capacity and reliability of dry vacuum pumps in modern semiconductor manufacturing processes have been constantly increasing. It is the reason that the costs for failed wafer batches and lost production times are higher and higher as the size of the production wafer is larger and larger. To tackle vacuum pump-related demands in the semiconductor production lines, Korean IC makers have recently put much efforts to establish the predictive maintenance and failure protection of vacuum pumps. For instance, Samsung has decided to buy no vacuum pump without the monitoring system for the pre-failure protection and predictive maintenance. This research team has surveyed what state variables are monitor in the Korean production lines and the current state-of-art of pump monitoring systems available from pump suppliers. This paper will introduce the surveyed results and will suggest what state variables a pump monitoring system should measure. Active ways of monitoring the change of selected state variables are proposed to assess the degradation of running pumps. To examine the effectiveness of the proposed methods, several field test results are demonstrated. Attempts of those field tests have allowed this research to see what limits current pump monitoring systems have. One of significant limits was the incompatibility to the SEMI equipment modeling and communication standards. The current monitoring systems were found to be too far from either SECS-II/GEM standards or the current e-Diagnostics guideline. Finally, this paper suggests a guideline for the vacuum pump manufacturers to meet for the integration of vacuum pumps into the computer-based management system.

VT-TuP7 Effect of a Depth of a V-shaped Groove of Substrate Keeping Adsorption Layer on Sliding in a Vacuum*, **A. Kasahara**, M. Goto, M. Tosa,* National Institute for Materials Science, Japan

We found that materials with a surface roughness around 100nm can offer as smooth sliding in a vacuum as at atmospheric pressure, and have also studied relation between direction of sliding probe and generated friction force. Results showed a decrease in friction force under optimum combination conditions that surface roughness of substrate was smaller than that of probe with surface roughness about 100nm and also showed that V-shaped groves line patterns of substrate and sliding probe cross each other at right angles. It is considered that smooth sliding might arise from absorption gas layer of the V-shape groove kept strongly. We therefore prepared V-shaped grooves with different heights for type 304 austenitic stainless steel sheets and studied a form of adsorption gas layer on the V-shaped groove of substrates to understand the effect of the grove on adsorption layer acting as a vacuum lubricant. Structure of the V-shaped groove such as height, open-angle and shape were analyzed by an atomic force microscopy (AFM) at an atmosphere. Cross-section of form adsorption layer on the V-shaped groove was then calculated by difference in pull-off distance from force curve diagrams obtained with AFM. Cross-section form of adsorption layer and the structure of the V-shaped groove were drastically changed by the structure depth. The structure of the V-shaped groove at a depth less than 120nm seemed to be satisfied with condition that absorption layer was trapped strongly. It is therefore concluded that the V-shaped groove at a depth about 100nm is ideal modified surface for satisfy adsorbed gases that can act as good vacuum lubricant because of exhibiting as low friction in a vacuum as friction at an atmospheric pressure.

VT-TuP8 Pumping Characteristics of Activated Alumina for Ortho- and Para-Hydrogen Molecules*, **T. Okano**, K. Niki, K. Yoshida, T. Ito, K. Fukutani,* University of Tokyo, Japan

Hydrogen is the most dominant gas species in ultrahigh vacuum. With respect to the nuclear spin state of hydrogen molecules, the triplet nuclear spin states are called ortho hydrogen (o-H@sub 2@) and the singlet ones are called para hydrogen (p-H@sub 2@). Since the spontaneous transition between a triplet and a singlet nuclear spin state is very small in gas phase, they are considered to be two distinct molecular species. In the present study, we studied on the behavior of o-H@sub 2@ and p-H@sub 2@ in a vacuum chamber. The apparatus consisted of a stainless steal chamber equipped with a mechanical compressor type cryohead. The lowest attainable temperature of the cryohead was 6 K. A small vessel (diameter: 10 mm, depth: 2 mm) was attached on the end of the cryohead and was filled with granules of activated alumina. The state-selective measurement of o-H@sub 2@ and p-H@sub 2@ was made by (2+1) resonant-enhanced multiphoton ionization (REMPI) method. Due to the requirement of antisymmetry of the total wave function of hydrogen molecules, even rotational state J is only allowed for o-H@sub 2@ and odd J-state for o-H@sub 2@. The J-state selective measurement by REMPI made it possible to detect o-H@sub 2@ and p-H@sub 2@ with very high sensitivity. The REMPI laser pulses with a wavelength of 201nm and an energy of 0.4 mJ/pulse is focused at the center of a radiation shield surrounding the activated alumina vessel. The ionized H2 is detected by a microchannnel plate attached to the radiation shield. After admitting hydrogen up to 2x10@super â?"4@ Pa, we started to cool down the temperature of the activated alumina. The densities of o-H@sub 2@ and p-H@sub 2@ in the chamber decreased rapidly at a temperature of 29 K and 25 K, respectively. This deference in the pump-down behavior was ascribed to the deference in the activation energy of desorption of ortho and para H@sub 2@.

VT-TuP10 A Summary and Status of the SNS Ring Vacuum Systems **, H. Hseuh,* Brookhaven National Laboratory*; **M. Mapes**,* Brookhaven National Laboratory, usa*; l. Smart, D. Weiss, J. Rank, R. Todd,* Brookhaven National Laboratory

The Spallation Neutron Source (SNS) ring is designed to accumulate high intensity protons. The vacuum system consists of the High Energy Beam Transport (HEBT) line, Accumulator Ring and the Ring to Target Beam Transport (RTBT) line. The accumulator ring has a circumference of 248m with 4 arcs and 4 straight sections while the RTBT and HEBT have a total length of 350m of beam transport line. Ultrahigh vacuum of 10-9 Torr is required in the accumulator ring to minimize beam-residual gas ionization. To reduce the secondary electron yield (SEY) and the associated electron cloud instability, the ring vacuum chambers are coated with Titanium-Nitride (TiN). In order to reduce radiation exposure quick disconnect chain clamp flanges are used in some areas where radiation levels are expected to be high. This paper describes the design, fabrication, assembly, and vacuum processing of the ring and beam transport vacuum systems as well as the associated vacuum instrumentation. *Work performed under the auspices of the U.S. Department of Energy.

VT-TuP11 Improvement of Materials Surface Properties by RF Glow Discharge Treatment*, **T.B. Huang**, X. Chen, X.Q. Tian,* Tsinghua University, P.R. China*; L.Z. Cha,* Tsinghua University, P.R. China, China

Glow discharge treatment is not only an effective means to remove the absorbed gases and impurity, but also an important tool to improve the materials surface properties in vacuum and electronic applications. Anyway, it can shorten the pump-down time when the system or devices are not permitted to carry out high temperature baking. Especially, the production of the longeval ultra-high vacuum environment is difficult in small volume so that it is a desirable means of glow discharge treatment. In the electronic applications, the rough surface is not desirable due to unexpected discharge occurring. Then, it is necessary to use some surface treating means, such as glow discharge treatment, which could make materials surface smooth in a certain scale. For some insulator, RF discharge is a good solution. However, special ultra high vacuum and electronic applications enlarge the difficulties of glow discharge treatment process. For meeting the complicated demands, its influence on materials surface properties is necessary to investigate. The RF glow discharge treatment experiments have been carried out for improving the materials surface properties in vacuum and electronic applications. The surface morphology and outgassing rate were studied under different glow discharge treatment. The key process parameters were the cleaning power, pressure, time, and so on. It could be known by experiments that the roughness of materials surface varied due to glow discharge treating process. The experimental results revealed that the outgassing rates of different gases decrease due to glow discharge treatment. The clean and smooth surface in nanometer scale for materials was obtained after the glow discharge treatment. The evacuating properties for materials became better due to the glow discharge treatment. Different bombardment ions were applied in the experiments, and the outgassing trend induced by ion bombardment was discussed in this paper.

VT-TuP12 Electron Stimulated Desorption of Hydrogen Physisorbed on a Cold Cupper Surface*, S.-S. Hong,* Korea Research Institute of Standards and Science, Republic of Korea*; M. Shoaib,* Pakistan Vacuum Society*; Y.-H. Shin,* Korea Research Institute of Standards and Science*; K.-H. Chung,* Korea Research Institute of Standards and Science, Korea*; I. Arakawa,* Gakushuin University, Japan

Study of hydrogen is indispensable in vacuum technology for extreme high vacuum (XHV). XHV can only be achieved by minimizing the hydrogen outgassing from the materials used in vacuum system. Outgassing phenomena can be classified into four categories by the combination between the source (chemisorbed or physisorbed species) and the process (thermal or electronic desorption). We have been investigating the electron stimulated desorption at the cold surface on which hydrogen is physisorbed in order to clarify the fundamental process of outgassing from a cryopump which is exposed to charged particles or radiation. An experimental system was constructed in the Korea Research Institute of Standards and Science (KRISS). The system consists of a UHV chamber, two turbomolecular pumps and a dry pump, a residual gas analyzer, an electron gun and a micro channel plate for ion detection. The time of flight spectrum of the desorbed ions is obtained using a multi channel scaler. ESD yields of the H+ ion were systematically measured as a function of H2 pressure upon the cold surface and the amount of adsorption of H2.

VT-TuP13 High Temperature Outgassing Tests on Materials Used in the DIII-D Tokamak*, K.L. Holtrop, M.J. Hansink,* General Atomics

This paper is a continuation of previous work on determining the outgassing characteristics of materials used in the DIII-D magnetic fusion tokamak.@footnote 1@ In order to achieve high performance plasma discharges in the DIII-D tokamak, impurity levels must be carefully controlled. Among the techniques used to control impurities are routine bakes of the vacuum vessel to an average temperature of 350°C. Materials used in DIII-D must not release any impurities at this temperature that could be transferred to the first wall materials and contaminate plasma discharges. To better study the behavior of materials proposed for use in DIII-D at elevated temperatures the initial outgassing test chamber was modified to include independent heating control of the sample and a simple load-lock chamber. The goal was to determine not only the total outgassing rate of the material under test but to also determine the gas species composition and to obtain a quantitative estimate of the removal rate of each species by the use of a residual gas analyzer. Initial results for aluminum anodized using three different processes, stainless steel plated with black oxide and black chrome, and a commercially available fiber optic feedthrough will be presented. This work was supported by the US Department of Energy under DE-FC02-04ER54698. @FootnoteText@ @footnote 1@K. Holtrop, J. Vac. Sci. Technol. A 17, 2064 (1999).

VT-TuP14 Photon Stimulated Desorption (PSD) and Secondary Electron Measurements of a Titanium Nitride Coated Copper Beam Chamber for the KEKB Collider@footnote 1@*, C.L. Foerster,* Brookhaven National Laboratory, US*; C. Lanni,* Brookhaven National Laboratory*; K. Kanazawa,* High Energy Accelerator Research Organization, Japan

KEKB is an asymmetrical collider operated by the High Energy Accelerator Research Organization (KEK) in Ibaraki, Japan. The collider utilizes two UHV ring chambers, one for a 3.5 GeV positron beam and the other for an 8 GeV electron beam, to study B-mesons. An electron cloud instability occurs at high currents which limits high current operation and reduces beam luminosity. To study a possible solution, which would reduce or eliminate the electron cloud, the inner surface of a one (1) meter long sample KEKB copper beam chamber was titanium nitride coated and studied on beamline U9a at the National Synchrotron Light Source (NSLS). The sample chamber has a circular cross section of 94mm inner diameter. The sample was installed in the U9a beam line and exposed to approximately 2.3X10@super+23@ photons directly from the source at a critical energy of 595 eV, striking the sample at an incident angle of 100mrad. Next, the TiN surface of the sample chamber was Argon Glow Discharge conditioned with approximately 2X10@super+18@ ions per square centimeter. After the conditioning the photon exposure was re-started and the measurements continued. The major PSD yields for hydrogen, carbon monoxide, carbon dioxide, methane, water vapor and photo-electron production are reported as a function of accumulated photon flux and sample preparation. The results are compared with previous PSD measurements on NSLS beam lines and those of other laboratories published for copper and TiN coated copper. @FootnoteText@ @footnote 1@ Work performed under auspices of the U.S. Department of Energy, under contract DE-AC02-98CH10886.

VT-TuP15 Results of Vacuum Pump Oil Testing to Minimize Oil Waste After More Than Two Years of Evaluation at the National Synchrotron Light Source*, C.L. Foerster,* Brookhaven National Laboratory, US*;* ***E-P. Hu****, E. Haas,* Brookhaven National Laboratory

This oil-testing project was established two and a half years ago to determine if synthetic vacuum pump oil could be used effectively to reduce some of oil waste produced during normal operation of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). More than two hundred oil-sealed rotary vane pumps are currently used at the NSLS facility, such that a longer oil change interval would greatly reduce maintenance costs as well as oil waste. Prior to this project the mechanical vacuum pump oil waste was approximately 75 gallons per year. Two basic types of vacuum pump oils, mineral and synthetic, are being tested for a direct comparison. Three two-stage mechanical pumps were set up and run simultaneously. Convectron gauges, cold cathode gauges, and isolation valves were connected to a central vacuum chamber with a common inlet pressure control and an RGA sampling valve. To simulate long-term mechanical pump operation, the system gas load was controlled at an inlet pressure of 500 mTorr using an air bleed valve. Vacuum pump oil suppliers to expedite the oil viscosity change, acid buildup, and pump-wear debris production suggested the inlet pressure. At this inlet pressure any oil back streaming is minimized. After two and a half years of running there have been no significant changes in either of the oil types. The detailed test data for the resulting oil properties, oil degradation, visual comparison, vacuum conditions, and pump characteristics will be presented for comparison of the pump oils used at NSLS and for estimation of the resulting oil waste reduction. @FootnoteText@ @footnote 1@ Work performed under the auspices of the U.S. Department of Energy, under contract DE-AC02-98CH10886.

Applied Surface Science
Room 206 - Session AS-WeM
Essential Tools for Surface Analysis

Moderator: J.E. Fulghum, University of New Mexico

8:20am **AS-WeM1 TOF-SIMS: Accurate Mass Scale Calibration***, F.M. Green,* ***I.S. Gilmore,*** National Physical Laboratory, UK*; M.P. Seah,* National Physical Laboratory, UK, United Kingdom

A study is presented of the factors affecting the calibration of the mass scale for TOF-SIMS. At the present time, analysts achieve a mass accuracy of only 150 ppm for large molecules (647 amu) and for smaller fragments of < 200 amu may typically be 60 ppm. The instrumental stability is 1 ppm and better than 10 ppm is necessary for unique identification of species. In the recent interlaboratory study@footnote 1@ only 3 instruments out of 32 were within 10 ppm for smaller fragments. The experimental uncertainty can lead to unnecessary confusion where peaks are wrongly identified or are ambiguous. Here we study in detail the instrumental parameters of a popular reflection TOF-SIMS. The effect of the ion kinetic energy, emission angle and other physical and instrumental operating parameters on the measured peak position are determined. This clearly shows why molecular and atomic ions have different mass accuracy and peak shapes. These data provide the basis for a coherent procedure for optimising the instrumental settings for accurate mass calibration and rules by which inorganics and organics may be incorporated. This leads to generic sets of ions for mass calibration, which, used for re-calibration, improves the mass accuracy of the interlaboratory study data@footnote 1@ by up to a factor of 4. Now, 12 instruments out of 32 are within the 10 ppm range. The effects of extrapolation beyond the calibration range are discussed and a recommended procedure given to ensure that accurate mass of large molecules is achieved within a selected uncertainty. One bonus of this study is that the instrument can now be operated in a regime with good energy discrimination to study the fragmented energies of molecules. We shall discuss how this compares with data from G-SIMS@footnote 2@ and supports the G-SIMS concept. @FootnoteText@ @footnote 1@ I S Gilmore, M P Seah and F M Green, submitted Surf. Interface Anal.@footnote 2@ I S Gilmore and M P Seah, Appl. Surf. Sci., 161 (2000), p. 465.

8:40am **AS-WeM2 Quantitative XPS: Quadrupole Terms, Shake-Up, Shirley Background and Relative Sensitivity Factors***,* ***M.P. Seah,*** National Physical Laboratory, UK, United Kingdom*; I.S. Gilmore,* National Physical Laboratory, UK

An analysis is provided of the XPS intensities measured in the NPL XPS database for 46 solid elements. This present analysis does not change the previous conclusions concerning the excellent correlation between experimental intensities following deconvolution using the angle-averaged REELS data and the theoretical intensities involving the dipole approximation and Scofield's cross sections. Here, we test the more recent calculations for cross sections by Trzhaskovskaya et al with quadrupole terms and find that their cross sections diverge from the database by up to a factor of 2. The quadrupole angular terms lead to small corrections also evaluated in the present analysis. Measurements of the extent of shake-up for the 46 elements broadly agree with theoretical calculations but details of the observed element-to-element variation are not reproduced in those calculations. The predicted theoretical constancy in the shake-up contribution implies that the use of the Shirley background will lead to a peak area that is a constant fraction of the true peak area including the shake-up intensities. If this were the case, the peak areas using the Shirley background would be a valid measure of intensity. We would therefore expect that the ratio of the peak area using the Shirley background to the intensity calculated using the cross sections, etc, would be a constant value, less than unity, with a reasonably small scatter. Unfortunately, the variability of the shake-up contribution, and the variability with which the Shirley background reproduces the angle-averaged background under the peak, itself, both combine to leave a 38% relative standard deviation in this ratio. The Shirley background thus appears to be a poor method for general quantitative analysis. Its use may need to be limited to specific situations where the sensitivity factors have been obtained from reference samples similar to those being analysed.

9:00am **AS-WeM3 SURFACE SCIENCE SPECTRA: The AVS Surface Science Database for the Surface Spectroscopy Community***,* ***S.W. Gaarenstroom,*** General Motors R&D Center **INVITED**

The surface spectroscopy community shares high-quality spectral data on hundreds of materials by means of the AVS Surface Science Database. Most of the shared spectral data is obtained by x-ray photoelectron spectroscopy, but Auger electron spectroscopy, secondary ion mass spectrometry, electron energy loss spectroscopy and other techniques are also represented. This database effort, named SURFACE SCIENCE SPECTRA, was launched in 1992. The SSS developers benchmarked and built upon the database efforts made for other kinds of spectroscopies (such as infrared spectroscopy, mass spectrometry, and x-ray diffraction), but were also attentive to the special needs in the surface science community. The contributors to the spectral database are from the worldwide surface science community at large (more than 450 individual contributors from more than 110 different institutions). The evaluators of the database are also from the entire surface science community, because all data records are peer-reviewed prior to acceptance and entry into the database. Simultaneous with the launch of the journal product of the SURFACE SCIENCE SPECTRA database, massive changes began in the publishing world's electronic technology and the individual scientist's preferences for accessing information. While the descriptors in each individual data record have changed only minimally in the years since the database launch, the delivery mechanism changed continually and will continue to change. The current conversion of the on-line journal to XML publishing technology provides new opportunities to inexpensively add useful features for the benefit of the database users.

9:40am **AS-WeM5 Software Package to Determine @epsilon@(k,@omega@) from Analysis of REELS***,* ***S. Tougaard,*** University of Southern Denmark, Denmark*; F. Yubero,* Inst. de Ciencia de Materiales de Sevilla, Spain

Engineering of new thin solid films of varying composition are of current high technological interest. Methods to determine the electronic properties of thin films are therefore of increasing importance. The complex dielectric function @epsilon@(k,@omega@) contains valuable information on the electronic structure. The effective single scattering cross section can be determined from analysis of reflected electron energy loss spectra (REELS)@footnote 1@ and a semi-classical dielectric response model for REELS was also developed.@footnote 2,3@ It has been shown how this can be applied to determine @epsilon@(k,@omega@) from analysis of experimental REELS. This provides an intesting technique because REELS is rather simple to apply, it is inexpensive, it is available in many laboratories and above all it can easily be applied to thin films of only a few nano-meters thickness grown on a supporting substrate. The complexity of the formulas has however been a hindrance for widespread use of the technique. To make it generally available, we decided to develop a software package with a user friendly graphical interface and interactive facilities. We hope that this tool will inspire more widespread use of this method to explore the electronic properties of solids and thin films. @epsilon@(k,@omega@) can also be used to make quantitative interpretation of the fundamental mechanisms in photo- and Auger electron spectroscopy and to calculate the inelastic mean free path for electrons in solids and determine the excitations that take place when the electron moves in the surface region or in the vacuum above the surface. The software, which is free of charge for non-commercial use, handles the theory developed in the following papers:. @FootnoteText@ @footnote 1@ S. Tougaard and I. Chorkendorff, Phys. Rev. B23 6570 (1987)@footnote 2@ F. Yubero and S. Tougaard, Phys. Rev B46, p. 2486 (1992)@footnote 3@ F. Yubero, J.M. Sanz, B. Ramskov and S. Tougaard, Phys Rev. B53, 9719 (1996).

10:00am **AS-WeM6 Complete Analysis of ToF-SIMS Spectral Images in a Research and Development Analytical Laboratory***,* ***V. Smentkowski,*** General Electric Global Research Center*; M. Keenan, J.A. Ohlhausen, P.G. Kotula,* Sandia National Laboratories

Time of flight secondary ion mass spectrometry (ToF-SIMS) spectral image raw data files contain a wealth of information since an entire mass spectrum is saved at each pixel in an ion image. Currently, few tools are available to assist the analyst in visualizing the entire raw data set and as a result, most of the measured data are never analyzed. Typically, the ToF-SIMS analyst manually selects a few species to monitor based upon input from the customer, knowledge of results obtained from similar past analysis, high peak intensity and/or unusual species detected in the spectrum. Manual analysis is complicated by the fact that little is known about real-life samples prior to analysis. The analyst is expected to perform rapid, cost effective, analysis and provide a complete description of the sample. Automated, non-biased, multivariate statistical analysis (MVSA) techniques are useful for converting the massive amount of data into a smaller number of components that are needed to fully describe the ToF-SIMS measurement. We are using AXSIA to perform MVSA on ToF-SIMS raw data files. The advantages of AXSIA include: the ability to select the mass range of interest, the ability to bin the mass spectra from 0.001amu to 1amu, optimal scaling of the data to account for Poisson counting statistics, and the generation of intuitive results. Examples will be selected to demonstrate these advantages. We will also demonstrate that positive ion and negative ion raw data files collected on the same region of a sample can be concatenated. MVSA analysis of the concatenated data provides a complete description of the sample. The analytical insight provided by concatenated MVSA analysis would be difficult, if not impossible, to obtain via other routes. Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

10:20am **AS-WeM7 Principal Components Analysis of TOF-SIMS Data: Why, What, and How*, D.J. Graham,*** University of Washington **INVITED**

Even the simplest TOF-SIMS spectrum can be complex. A typical spectrum may contain hundreds of peaks, the intensities of which can be correlated. This complexity has led to the exploration and application of multivariate analysis (MVA) methods to TOF-SIMS data in an attempt to simplify analysis and maximize the information content extracted from the data. MVA of TOF-SIMS spectra has shown promise and success for spectra and images across many systems including self-assembled monolayers, proteins, and polymers. Due to this success, multivariate analysis of TOF-SIMS data is quickly becoming more standard within the surface analysis community, yet there have been no standards set regarding how to properly apply multivariate methods to TOF-SIMS data. It is important to make sure that as progress continues in the application of MVA methods to TOF-SIMS data, standards be established in the application of theses methods, and that effort be made in the optimization of these methods, and the education of the community. This talk will highlight important considerations in the use of PCA with TOF-SIMS data. Experimental design, peak selection, data preprocessing and data interpretation will be discussed as it pertains to PCA of TOF-SIMS spectra.

11:00am **AS-WeM9 Automated Peak Identification in a TOF-SIMS Spectrum*, H. Chen*,** *E.R. Tracy, W.E. Cooke, M.W. Trosset,* College of William and Mary*; D. Malyarenko,* INCOGEN Inc.*; D.M. Manos,* College of William and Mary*; M. Sasinowski,* INCOGEN Inc.

Although the high mass resolution, imaging capability and the high-throughput capability of mass fingerprint measurements have made TOF-SIMS one of the standard tools for research in surface analysis. A bottleneck is that TOF-SIMS produces very large raw data sets that must be preprocessed to identify the mass peaks for further analysis, especially when complex biological samples produce a large number of peaks. The accuracy of the mass assignment, which is critical when comparing mass fingerprints with databases, can be another limitation. Under survey conditions, the positions of the desired mass peaks are commonly not known beforehand, and TOF-SIMS peak-picking requires a procedure to distinguish mass peaks from background noise. Often, those peaks and their positions are identified manually. This introduces a subjective error due to the asymmetric peak line shape and to Poisson (counting) noise which has larger variance at larger peaks. This results in a degradation of the apparent machine performance and an inconsistency in the peak identification. We have developed an automated peak picking algorithm based on a maximum likelihood approach that effectively and efficiently detects peaks in a TOF-SIMS spectrum. The algorithm takes into account the underlying characteristic Poisson process and asymmetric peak line shape and produces maximum likelihood estimates of peak positions and amplitudes. It also simultaneously develops estimates of the uncertainties in each of these quantities. With this approach, we avoid the ambiguities involved in manual peak picking and mass assignments. We use the estimated peak positions, amplitudes and their uncertainties to align different spectra more accurately than is possible by using a few known calibrants. This precise peak summary is crucial for further multivariate analysis.

11:20am **AS-WeM10 More Information from Shorter Acquisition Times in XPS Imaging and Other Multivariate Surface Analytical Datasets*, P.J. Cumpson,*** National Physical Laboratory, UK

Quantification of multivariate datasets, such as XPS images, is a major area of research due to the impressive capability of modern instruments. It can, however, present challenges in terms of signal-to-noise and long acquisition times. A very simple but computationally-intensive Bayesian chemometric method@footnote 2@ for addressing this problem was published around ten years ago. With increasing personal computer speeds this has become not just more practical, but even very rapid today. This approach to electron counting statistics results in a novel quantification method that halves acquisition time, or equivalently, results in an increase in signal-to-noise of roughly a factor of 1.4, rising to 1.7 for the shortest acquisition time, noisiest images. This is not a ``black box'' statistical method, but a relatively simple way of building-in the assumption that the primary beam is fairly stable from pixel-to-pixel, which is certainly the case for modern XPS instruments. The method is potentially valuable in depth-profiling too. We show that combining this method with rapid Monte Carlo methods@footnote 3,4@ (whose routine use has also become much more practical recently) leads to several important new chemometric methods for count-limited, multivariate surface analytical data in general. @FootnoteText@ @footnote 1@ K Artyushkova and J E Fulghum in "Surface Analysis by Auger and X-ray Photoelectron Spectroscopy", Ed. D Briggs and J T Grant (IM Publications, Chichester UK, 2004).@footnote 2@ P J Cumpson and M P Seah, Surface and Interface Analysis, 18 (1992) 361.@footnote 3@ P J Cumpson, Surface and Interface Analysis 20 (1993) 727.@footnote 4@ D Ze-jun and R Shimizu in "Surface Analysis by Auger and X-ray Photoelectron Spectroscopy", Ed. D Briggs and J T Grant (IM Publications, Chichester UK, 2004). .

11:40am **AS-WeM11 Improvements in the Spatial and Spectral Resolution of X-ray Photoelectron Images through Multivariate Analysis and Multisensor Fusion*, K. Artyushkova,*** *J.E. Fulghum, L.R. Williams,* The University of New Mexico*; S.J. Hutton, S.J. Coultas,* Kratos Analytical Ltd., UK

Improvements in spectral and spatial resolution of imaging X-ray photoelectron data are of growing importance, as the chemical complexity of materials under study increases, and the size of features to be resolved decreases. In this work we use a combination of multivariate analysis methods (MVA) and multisensor image fusion to resolve photoelectron image features in components that are similar in chemistry and small in size, relative to the spatial resolution of the technique. Methods combining XPS image acquisition schemes with multivariate analysis were tested to facilitate analysis of multicomponent samples containing spectrally overlapped chemical components. Additional spatial distribution information can potentially by obtained through multisensor image fusion of atomic force microscopy (AFM) and XPS images. X-ray photoelectron spectroscopy (XPS) has a high energy resolution but relatively low spatial resolution. In contrast, AFM images have significantly higher spatial resolution. We report initial efforts to combine low resolution color images (XPS) and a high resolution monochromatic images (AFM) to produce a higher spatial resolution XPS images. The validity of these approaches will be demonstrated using patterned SAM samples with known chemistry and spatial morphology. Application of these methods will be shown using images from phase-separated polymer blends. This work has been partially supported by NSF CHE-0350666 and UNM.

Biomaterial Interfaces
Room 311 - Session BI1-WeM

Protein-Surface Interactions

Moderator: M. Textor, ETH Zurich, Switzerland

8:40am **BI1-WeM2 Functionalization of Diamond and Silicon Surfaces with Molecular Monolayers to Control Protein-Surface Interactions***, T. Lasseter Clare, B. Clare, N. Abbott, B.M. Nichols,* ***R.J. Hamers,*** University of Wisconsin-Madison

We have investigated the chemical functionalization of diamond and silicon surfaces with short ethylene glycol (EG) oligomers to control the the nonspecific adsorption of proteins to these surfaces. EG oligomers bearing a terminal vinyl group were linked to H-terminated surfaces of diamond and silicon using illumination with ultraviolet light at 254 nm. The resulting layers were characterized by XPS, and the effects of EG oligomers on binding of avidin, casein, fibrinogen, and BSA were qualitatively investigated using on-chip fluorescence measurements. To avoid issues related to fluorescence quenching and facilitate quantitative comparison on different materials, we measured avidin adsorption using an elution method. These experiments show that EG-modified surfaces of nanocrysalline diamond, single-crystal silicon, and polycrystalline gold films all resist binding of avidin to nearly the same extent. One of the attractive features of diamond is its extraordinary chemical stability. In a comparison of EG-modified surfaces of diamond, silicon, and gold, we find that gold and silicon samples undergo a significant degradation over a time period of approximately 1 week, while EG-diamond samples undergo no detectable change. These results are corraborated with XPS measurements that show silicon and gold undergo partial loss of their functionalization layers, while EG-diamond shows no measurable change. The effects of surface roughness were investigated by comparing EG-modified surfaces of nanocrystalline, polished, and cleaved single-crystal diamond. The influence of monolayer termination and other factors will also be presented. Overall, these measurements show that photochemical modification of Si and diamond with vinyl-terminated EG oligomers is a very effective way to reduce nonspecific adsorption. They also provide new molecular insights into the factors the control protein adsorption at surfaces.

9:00am **BI1-WeM3 The QCM-D Technique for Control of Protein Binding on Nanoscale LSPR Active Substrates***, **F. Höök,*** Lund University, Sweden **INVITED**

In the search for surface modifications that minimizes the influence on the structure and function of adsorbed proteins, supported phospholipid bilayers (SPBs) have been proven inert towards protein adsorption from as complex mixtures as serum. Since they at the same time fulfils the requirements set on specific coupling of both water-soluble and membrane bound proteins, have made them attractive in various biosensor applications and as coatings for biomaterials. However, so far limited progress has been made with respect to SPB formation on nanoscale solid supports. By utilizing insights gained from quartz crystal microbalance with dissipation (QCM-D) monitoring of protein/lipid interactions on either Au or SiO2, we have established a surface-modification protocol that enables localized rupture of phospholipid vesicles on SiO2 in the bottom of nanometric holes in a thin Au film. The hole-induced localization of the localized surface plasmon resonance (LSPR) field to the voids of the holes is demonstrated to provide a novel concept for studies of protein-binding reactions confined exclusively to SPB-patches supported on SiO2.@footnote 1@ In particular, we emphasize the possibility to in this way perform label-free studies of lipid-membrane mediated reaction kinetics, including the compatibility of the assay with array-based recording, with signals originating from bound protein in the sub-zeptomole regime. Extensions of this concept includes the use of the conductive LSPR hole substrate (i) as one of the electrodes of the QCM-D sensors, enabling simultaneous QCM-D and LSPR readouts of reactions occurring on, for example, either Au or SiO2, and (ii) for studies of protein binding to individual colloidal particles that match the size of the holes. @FootnoteText@ @footnote 1@Svedhem S, Pfeiffer I, Larsson C, Wingren C, Borrebaeck C, Höök F. ChemBioChem 2003:339-343. @footnote 2@Dahlin A, Zach M, Rindzevicius T, Kall M, Sutherland DS, Hook F. JACS 2005, 127:5043-5048.

9:40am **BI1-WeM5 In Deuterated Water the Unspecific Adsorption of Proteins Is Significantly Slowed Down: Results of an SPR-study using Model Organic Surfaces***, **Chr. Grunwald,*** Ruhr-University, Germany*; J. Kuhlmann,* Max-Planck-Institute for Molecular Physiology, Germany*; Ch. Woell,* Ruhr-University, Germany

The control of unspecific adsorption of proteins to natural and technical surfaces plays an important role in biology and also for many applications. Organic model surfaces e.g. self-assembled monolayers, are often used to identify fundamental surface and/or protein properties that rule protein adsorption.@footnote 1@ Some techniques involved in biointerface research require the use of heavy water, e.g. neutron scattering techniques.@footnote 2@ Also in NMR studies D@sub 2@O is the solvent of choice when focusing on biomolecular and hydration dynamics. So far several studies have been concerned with the characterization of the unspecific adsorption of proteins from normal water buffers.@footnote 3@ In the present work we report a comparison of the unspecific protein adsorption from normal and heavy water buffers. Previously it has been assumed that the surface kinetic of the unspecific adsorption is unaffected by the substitution of water by D@sub 2@O.@footnote 2@ However, for the four proteins investigated here this assumption does not hold. The ratio k@sub H@/k@sub D@ of the adsorption rate constants of the different buffer conditions describe the strength of the isotope effect. We have measured ratios between 1.0 and 2.6 indicating that the adsorption kinetics are strongly affected by a H@sub 2@O-D@sub 2@O-substitution. @FootnoteText@ @footnote 1@Herrwerth, S.; Eck, W.; Reinhardt, S.; Grunze, M. Journal of the American Chemical Society 2003, 125, 9359-9366.@footnote 2@Schwendel, D.; Hayashi, T.; Dahint, R.; Pertsin, A.; Grunze, M.; Steitz, R.; Schreiber, F. Langmuir 2003, 19, 2284-2293.@footnote 3@Ostuni, E.; Grzybowski, B. A.; Mrksich, M.; Roberts, C. S.; Whitesides, G. M. Langmuir 2003, 19, 1861-1872.

10:00am **BI1-WeM6 The Development of Molecular Simulation Capabilities as a Tool to Understand Protein Adsorption Behavior at the Molecular Level***, F. Wang, Y. Sun, S.J. Stuart, **R.A. Latour,*** Clemson University

Although important, the molecular mechanisms involved in protein adsorption processes are still not well understood. Empirical force field-based molecular simulation methods have been successfully developed to enable molecular mechanisms to be studied for other applications, such as protein folding and ligand-receptor binding; these methods have similar potential to help elucidate the molecular mechanisms for protein adsorption. Two of the most important problems that must be addressed before methods can be developed for this application are the force field problem and the sampling problem. The force field problem relates to the design of the energy function and its parameters that control how atoms interact with one another during a simulation. The sampling problem relates to the need to sample molecular events over timeframes that extend far beyond those that are capable of being reached using standard molecular dynamics methods. The objective of our research is to develop computational methods to address both of these issues, with an initial focus on the development of methods to calculate the free energy of peptide adsorption. In conventional simulations, peptides become stuck in low-energy conformations and this prevents adsorption free energy from being accurately calculated. We are therefore developing biased-sampling methods to enable adequate conformational space to be sampled in peptide-surface simulations so that adsorption free energy can be properly calculated. With this capability, the accuracy of a protein adsorption force field can be evaluated, modified, and validated by comparison between calculated adsorption free energy and experimentally measured values.

10:20am **BI1-WeM7 Model Dielectric Functions for Adsorbed Protein Layers***, **H. Arwin,*** Linköping University, Sweden*; J.A. Woollam, D.W. Thompson,* University of Nebraska, Lincoln

A detailed knowledge about protein-surface interactions is of crucial importance for development of biomaterials, bioanalytical tools and biosensors as well as for understanding the mechanisms in protein-cell interactions. Ellipsometry is extensively used in these areas due to its nm-resolution in layer thickness and capability for in situ studies at solid-liquid interfaces. The outputs from an ellipsometer study are typically quantification of adsorbed surface mass and/or dynamics of protein adsorption. Recently also infrared ellipsometry has become available and optical signatures like amide bands in surface-bound proteins can be quantified. However, for layers of nm thickness, the analysis is not straight forward and it can be hard to separate thickness and refractive index of the protein layer, especially with single wavelength ellipsometry data. Spectroscopic ellipsometry can in some cases resolve this but very few studies are reported. Another major advantage if spectroscopic data are available is the possibility to model, i.e. to parameterize the wavelength dispersion of the refractive index. This also leads to noise reduction. In this report a model dielectric function (MDF) concept for protein layers is proposed. Notice that the square root of the MDF equals the refractive index. The MDF is based on a Cauchy dispersion to which Lorentzian and/or Gaussian resonances are added to account for electronic and vibrational excitations in ultraviolet/visible and infrared spectral regions, respectively. The use of the proposed MDF is exemplified on fibrinogen adsorbed on gold. With variable angle spectroscopic ellipsometry, data were recorded in the spectral region 0.2 to 30 µm (300-5000 cm@super-1@) before and after protein adsorption. In the analysis the fibrinogen layer thickness is obtained as well as the refractive index (the square root of an MDF) and the amide bands I, II and A are resolved. A generalization to protein layers in general will be discussed.

10:40am **BI1-WeM8 Protein Nanopatterning onto Nanostructured Polymer Surfaces***, **C. Satriano,** G.M.L. Messina, G. Marletta,* University of Catania, Italy

The preferential adsorption of human fibronectin, lactoferrin, serum albumin and lysozime has been investigated onto nanostructured polysiloxane surfaces obtained by a colloidal crystal-based technique in combination with cold plasma treatment. In particular, 2D arrays of nanopores, having typical dimensions of about 55 nm of diameter and about 3 nm and 1 nm respectively for the rim height and the pore depth were fabricated. Polystyrene nanoparticles were used to imprint regularly-spaced nanopores within a bilayer formed by an untreated polysiloxane film onto a plasma-modified one. The internal area of the pores consisted of hydrophilic O@sub 2@-plasma treated polysiloxane, while the external surface was the hydrophobic untreated polymer. The spatially-resolved features of adsorbed proteins were investigated by means of Atomic Force

Microscopy. The in situ adsorption process on homogeneously modified surfaces has been investigated by means of Quartz Crystal Microbalance with Dissipation Monitoring, while X-ray Photoelectron Spectroscopy was employed to evaluate ex-situ the coverage and thickness of the protein adlayers for the two types of surfaces. The results showed that the relevant chemical factors are the surface free energy and the chemical termination of the different surfaces. In particular, human fibronectin and lactoferrin showed a preferential adsorption outside of the hydrophilic nanopores, while lysozime and human serum albumin seem prefer the nanopore area. The results suggest that it could be possible to achieve the separation of protein mixtures by a spatially resolved adsorption.

11:00am **BI1-WeM9 Immobilization of Protein Nano-Clusters on Polymeric Nano-Craters***, A. Valsesia, **P. Colpo**,* EC-JRC-IHCP Italy*; M. Lejeune,* EC-JRC-IHCP Italy, Italy*; F. Bretagnol, T. Meziani,* EC-JRC-IHCP Italy*; F. Rossi,* EC-JRC-IHCP Italy, Italy

The reduction of the typical length scale in the creation of patterned surfaces is of high interest in the field of bio-interacting materials and more particularly for biosensors design. For instance, the creation of sub-micrometric or nano-metric patterns is important for the miniaturization of the actual protein and DNA micro-spotting technology, or for the minimization of the non-specific absorption in biosensors, or to increase the orientation capability of immunosensors. To generate these patterned surfaces at the submicron level, the use of classical optical lithography methods becomes complex, since they are reaching the diffraction limits when the feature sizes are lower than 200 nm. Among the alternative techniques of lithography such as E-beam, nano-sphere lithography is a reliable method to produce nano-topography over large area surfaces. In this work we developed a reliable technique to produce polymeric nano-craters with bio-specific carboxylic functionalities and with controlled surface density and distribution, surrounded by an homogeneous matrix of anti fouling polymer. The process has been carried out combining plasma deposition and etching techniques with colloidal masking. The plasma etching process parameters have to be accurately studied in order to create the nano-structures without affecting their chemical properties. The micro-structural characterization of the nano-structured films was carried out by the combination of Ellipsometry, FT-IR spectroscopy and Atomic Force Microscopy (AFM). The surface chemical contrast at the nano-scale was characterized by using Chemical Force Microscopy. The creation of nano-patterned surfaces with controlled topography and chemistry at the sub-micron scale was demonstrated. In particular a contrast in the wettability between the two nano-regions was observed. The preferential absorption of the biomolecules inside the fouling nano-craters was demonstrated by Confocal Fluorescence Microscopy measurements.

11:20am **BI1-WeM10 Binding of the Streptococcal C5a Peptidase to Immobilized Fibronectin***, **J.R. Hull**,* University of Washington*; G. Tamura,* The University of Washington Dept. of Pediatrics*; D.G. Castner,* University of Washington

Group B Streptococci (GBS) are a leading cause of sepsis and meningitis in newborns, and an emerging cause of serious bacterial infections in immunocompromised adults and the elderly. The streptococcal C5a peptidase (ScpB) of GBS is found in virtually all clinical isolates of GBS. ScpB inhibits neutrophil chemotaxis by enzymatically cleaving the complement component C5a. ScpB is a known Fibronectin (Fn) adhesin; however, it only binds to immobilized Fn and not soluble Fn. Therefore, it is unknown whether or not ScpB binds to a conformational determinate of Fn or multiple adjacent Fn molecules. For this study, surface plasmon resonance (SPR) was used to determine the affinity of ScpB for immobilized Fn. The measured affinity is in the nM range, which is biologically significant. ScpB was tethered to an atomic force microscope (AFM) tip via the bifunctional cross linker pyridyldithio poly(ethylene glycol) succinimidylpropionate (NHS-PEG-PDP). Each step of the tip functionalization was verified by X-ray photoelectron spectroscopy, static secondary ion mass spectrometry, and infrared spectroscopy. Adsorbed Fn was imaged via intermittent contact AFM with the ScpB modified tip at varying surface concentrations. Then force-distance curves were used to measure the interactions between ScpB and adsorbed Fn.

11:40am **BI1-WeM11 Enzyme Adsorption as a Model System to Probe Adsorption-Induced Changes in Protein Bioactivity***, **K.P. Fears**, Y. Sun, R.A. Latour,* Clemson University

Although the control of the bioactivity of adsorbed proteins is recognized to be critical for the control of cellular response, little is known about the actual molecular mechanisms involved. Molecular simulation provides great potential to elucidate these mechanisms and to be developed as a tool for surface design to control the orientation, conformation, and bioactivity of adsorbed proteins. The development of accurate molecular simulation methods, however, is critically dependent on the development of experimental methods that can be used to isolate specific molecular events using protein-surface systems that are sufficiently simple to enable them to be represented in molecular simulations. The objective of this research is to experimentally develop model enzyme adsorption systems for this purpose. Homogenous alkanethiol self-assembled monolayers with various end group functionalities are being used in conjunction with surface plasmon resonance spectroscopy to measure the effect of adsorption on protein bioactivity using a set of small enzymes (e.g, lysozyme, trypsin) with known molecular structure, bioactive site, substrate, and native-state bioactivity. An adsorbed trypsin layer on a positively charged surface was measured to be approximately 96% active, only 5% active on a hydrophobic surface, and have no detected activity on a negatively charged surface. It is hypothesized that orientational and conformational effects are primarily responsible for the differences between the charged surfaces and the hydrophobic surface, respectively. Circular dichroism studies are planned to measure the secondary structures of the adsorbed proteins to support this hypothesis.

Biomaterial Interfaces
Room 312 - Session BI2-WeM

Biomembranes and Spectroscopy

Moderator: J. Hickman

8:20am **BI2-WeM1 Fabrication of Well Structures with Electrode by Synchrotron Radiation Etching and Formation of Lipid Bilayer Giga-Ohm Seals***, **Md. Rahman**,* The Graduate University for Advanced Studies, Japan*; R. Tero,* NINS, Japan*; Y.-H. Kim,* The Graduate University for Advanced Studies, Japan*; T. Yano, M. Aoyama,* NINS, Japan*; R. Sasaki, H. Nagai, M. Yoshida,* AISHIN SEIKI Co., Ltd., Japan*; T. Urisu,* NINS, Japan

Supported membrane is a lipid bilayer supported on solid surfaces, and is useful as an artificial cell membrane for the study of biological reactions of membrane proteins. We are developing supported membrane biosensors for the purpose of developing the new research tool of the cell membrane surface reactions. These devices are interesting also from the view point of the application to the large scale screening method for the new medicine development. We have established a technique to fabricate a well-type microelectrode with about 1 µm diameter on the surface of a SiO@sub 2@/CoSi@sub 2@/Si substrate. The SiO@sub 2@/CoSi@sub 2@/Si was covered by Co contact mask by sputtering deposition. The circle pattern was made on the Co mask using the femto-second laser ablation. The SiO@sub 2@ was etched by synchrotron radiation (SR) etching. SR was used because of its unique features such as high spatial resolution, extremely high material selectivity between CoSi@sub 2@ and SiO@sub 2@, low damage, and clean etching atmosphere. AFM images of the SiO@sub 2@ surface after the removal of the Co mask with 0.1 M HNO@sub 3@ aq. showed that the surface was very flat (R@sub a@=0.8 nm). Ag (50 nm) was deposited by electroplating on the CoSi@sub 2@ which is exposed at the bottom of the etched well. Then the surface of the Ag was coated with AgCl also by electroplating. A single planar lipid bilayer (DPPC : POPS = 90:10) was deposited on these microelectrodes by the rapture of giant unilamellar vesicles. From the I-V characteristics of the membrane, the resistance of the lipid bilayer was 1.2 G@ohm@. This value was larger enough for the single channel current measurement. The measured capacitance was 10.7 pF, which is larger than that estimated from the total electrode area. This may be due to that the charge is accumulated at the larger area of the lipid bilayer than the area of just the electrode holes by the current through the thin (1 nm) water layer under the lipid bilayer.

8:40am **BI2-WeM2 Probing Lipid Membrane Responses to Surface Morphology***, **S.D. Gillmor**, J.J. Heetderks, X. Wang, Q. Du, P.S. Weiss,* The Pennsylvania State University

The outer cellular membrane is a mixture of protein receptors, lipids and cholesterol whose organization is incompletely understood. Many cell membranes have complex interactions with the underlying basement membrane, and our investigations focus on lipid deformation due to adhesion to this support. We model the complex basement membrane structure chemically and topographically, through lithographically defined features for control over substrate morphology, and through chemical modification of the surface. Initially using simplified, lipid-only giant unilamellar vesicles (GUVs) as models, we probe the membrane behavior in response to surface topography. Biotin-labeled lipids allow us to tether the vesicles to the surface and to investigate the role of adhesion proteins in the deformation during the vesicle-surface interactions. From confocal microscopy, we image the profile of the vesicle on both planar and topographically patterned substrates. From our model system, we measure the lipid membrane deformation due to the topography, and we compare these findings with the line tension characterization in the literature.@footnote 1@ We model and categorize these responses in our simple system using phase field formulation and compare these findings to cell responses on topographically patterned surfaces. @FootnoteText@ @footnote 1@ Baumgart, Hess and Webb, (2003) Nature 425, 821.

9:00am **BI2-WeM3 Computer Simulation of Water-Mediated Force between Supported Phospholipid Membranes***, A. Pertsin,* University of Heidelberg, Germany*; **M. Grunze**,* University of Maine and University of Heidelberg, Germany

The grand canonical Monte Carlo technique is used to calculate the water-mediated force operating between two supported 1,2-dilauroyl-DL-phosphatidylethanolamine (DLPE) membranes in the short separation range. The intra- and intermolecular interactions in the system are described with a combination of an AMBER-based force field for DLPE and a TIP4P model for water. The long range contributions to the electrostatic interaction energy are treated in the dipole-dipole group-based approximation. The total water mediated force is analyzed in terms its hydration component and the component due to the direct interaction between the membranes. The latter is, in addition, partitioned into the electrostatic, van der Waals, and steric repulsion contributions to give an idea of their relative significance in the water-mediated interaction of the membranes.

9:20am **BI2-WeM4 Phospholipid Bilayers Nanomechanics***, G. Oncins, S. Garcia-Manyes, **F. Sanz**,* University of Barcelona, Spain

Mechanical properties of several phosphocholine supported planar bilayers deposited on mica have been tested in liquid environment by lateral force microscopy (LFM) and force spectroscopy. The presence of these bilayers has been detected topographically using atomic force microscopy (AFM). To test how the presence of NaCl affects the frictional properties of phospholipid bilayers, samples in saline media ranging from 0 M to 0.1 M NaCl were prepared. Changes in the lateral force vs. vertical force curves were recorded as a function of NaCl concentration and related with structural changes induced in the phosphatidylcholine bilayers by the presence of electrolyte ions. Three friction regimes are observed as the vertical force exerted by the tip on the bilayer increases. In order to relate the friction response with the structure of the bilayer, topographic images were recorded simultaneously to friction data. Ions in solution have proved to be able to screen charges present in phosphatidylcholine polar heads, leading to more compact bilayers.@footnote 1@ As a consequence, the vertical force at which the bilayer breaks while performing friction experiments increases with NaCl concentration.@footnote 2@ In addition, images show that low NaCl concentration bilayers recover more easily due to the low cohesion between phospholipid molecules. The vertical mechanical resistance of phosphatidylcholine bilayers has been tested with force curves,@footnote 3@ showing a discontinuity when the bilayer breaks under the pressure exerted by the tip. As expected, the force at which this breakthrough takes place increases with NaCl concentration, pointing out an increase of vertical and lateral mechanical stability induced by ions. @FootnoteText@ @footnote 1@Pandit,S.A.; Bostick, D.; Berkowitz, M. L. Biophys. J., 2003, 84, 3743.@footnote 2@Oncins,G.; Garcia-Manyes, S.; Sanz,F.; (sent 1st revision to Langmuir)@footnote 3@Garcia-Manyes,S.; Oncins,G.; Sanz,F.; (sent 1st revision to Biophys.J.).

9:40am **BI2-WeM5 Fabrication of Nanobiological Materials through Molecular Self-assembly***, **S. Zhang**,* Massachusetts Institute of Technology **INVITED**

Two complementary strategies can be employed in the fabrication of molecular biomaterials. In the 'top-down' approach, biomaterials are generated by stripping down a complex entity into its component parts. This contrasts with the 'bottom-up' approach, in which materials are assembled molecule by molecule and in some cases even atom by atom to produce novel supramolecular architectures. The latter approach is likely to become an integral part of nanomaterials manufacture and requires a deep understanding of individual molecular building blocks, their structures, assembling properties and dynamic behaviors. Two key elements in molecular fabrication are chemical complementarity and structural compatibility, both of which confer the weak and noncovalent interactions that bind building blocks together during self-assembly. Significant advances have been achieved at the interface of biology and materials science, including the fabrication of nanofiber materials for 3-D cell cultures, tissue engineering and regenerative medicine, the peptide detergents for stabilizing, and crystallizing membrane proteins as well as nanocoating molecular for cell organizations. Molecular fabrications of nanobiomateirals have fostered diverse scientific discoveries and technological innovations. Shuguang Zhang made a serendipitous discovery of self-assembling peptides from studying yeast protein, zuotin. He subsequently conceptualized, developed and commercialized diverse self-assembling peptide materials including peptide nanofibers, functional peptide ink, peptide molecular switches and antennae, peptide surfactants/detergents. These self-assembling peptides materials have a broad spectrum of uses, ranging from nanofiber scaffold hydrogel for 3-D tissue cell culture, tissue repair, tissue engineering and regenerative medicine; biochips for direct printing, anchoring and patterning molecules and cells; and peptides for solubilizing, stabilizing and crystallizing membrane proteins. Using systematic and molecular engineering approach, he and his students, postdocs and colleagues opened a new avenue to fabricate novel nanobiological materials from bottom up through molecular self-assembly.

10:20am **BI2-WeM7 1-dimensionally Crosslinked Intra- and Interleaflet Bilayers for Cell Surface Studies***, **R. Michel**, M. Halter, G. Sather, E. Naeemi, D.G. Castner,* University of Washington

Although supported lipid bilayers are increasingly used as model systems for biological coatings, they lack the high stability desired for use in ambient or ultrahigh-vacuum environment. Poly(hydroxyethyl methacrylate) (pHEMA) is a hydrogel used in many biomedical applications, most commonly in ophthalmic applications. By tethering lipid bilayers to a pHEMA support, we better mimic the natural environment of the implant. In this work, a twofold approach was employed to stabilize the supported lipid film to the pHEMA. The intra-leaflet stabilization is achieved by cross-linking part of the lipids via the hydrophobic tail using SH-dipalmitoylphosphatidylcholine (DPPC) /acryloyloxy-phosphatidylcholine. To stabilize the leaflet to the surface, dimyristoylphosphatidylethanolamine (DMPE) lipids are mixed with the intra-leaflet crosslinked lipids. The DMPE lipids are crosslinked to the pHEMA substrate via 1.1' carbonyldimidazole (CDI) activation of the pHEMA surface and attachment of the polar head group. Using X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), and fluorescence microscopy, we characterized the purity, composition, and degree of crosslinking of the bilayers. We find that use of these inter- and intra-leaflet crosslinking agents allow us to tailor the fluidity and rigidity of the supported lipid bilayers, which opens up new possibilities for protein incorporation and activity in these lipid bilayers.

10:40am **BI2-WeM8 A Method to Quantify and Evaluate the Efficiency of Nanometer-Sized Lipid Vesicle Modifications***, **I. Pfeiffer**,* Chalmers University of Technology, Sweden*; F. Höök,* Lund University, Sweden

We recently demonstrated a DNA-hybridization-based concept for site-selective and sequence-specific sorting of lipid vesicles on DNA arrays.@footnote1@ By utilizing bivalent cholesterol-based coupling of oligonecleotides to lipid membranes, we showed that the coupling was irreversible in a broad concentration range on planar supported phospholipids bilayers (SPBs) and that exchange between differently modified vesicles in a suspension was sufficiently low to provide efficient sorting. In order to evaluate in further detail the efficiency of this and other lipid vesicle modification protocols, we present in this work a generic method that provides a simple means of quantifying the modification in terms of number of molecules per lipid vesicle. By exposing an SPB to a mixture of cholesterol-modified DNA and lipid vesicles, the amount of free DNA, i.e. DNA not anchored to the lipid vesicles, can be estimated by recording the initial rate of binding to the supported membrane. By comparing the so obtained response with a calibration curve based on the initial rate of binding from suspensions of free DNA, it was demonstrated that the efficiency of the bivalent coupling was 100% in the range of <1 to 35 oligonucleotides per vesicle - thus demonstrating a high stability and efficiency of this particular coupling. The generic value of the method for other types of modifications was demonstrated using cholera toxin binding to GM1 modified lipid vesicles, and given that a solid support can be made inert to colloidal particles, the method holds great promise to be generic for any type of modification scheme. @FootnoteText@ @footnote1@Pfeiffer, I.; Hook, F. Journal of the American Chemical Society 2004, 126, 10224-10225.

11:00am **BI2-WeM9 Mapping Protein Dynamics in Living Cells using Two-Photon Image Correlation Spectroscopy*, P. Wiseman,*** McGill University, Canada **INVITED**

We will present recent advances in image correlation methods and their application for measurements in living cells. The talk will focus on the development of image correlation spectroscopy (ICS) as an imaging extension of fluorescence correlation spectroscopy (FCS). The ICS technique is ideally suited to measure transport and clustering of fluorescently tagged proteins in cellular membranes where transport is slow and static proteins abound. The image correlation methods are based on the measurement of fluorescence intensity fluctuations as a function of space and time in cells collected as image time series using a laser scanning microscope (either confocal or two-photon). Spatial and temporal variants of the basic ICS method will be introduced and the power of these approaches to measure both aggregation and transport of cell surface proteins will be explained with the aid of computer simulations to demonstrate the measurement detection limits. The use of two-photon microscopy to perform image cross-correlation spectroscopy (ICCS) studies will also be discussed. ICCS allows direct measurement of the interactions of two co-localized proteins labeled with fluorophores having different emission wavelengths even in a high density environment. The transport properties of the co-localized proteins are also measured simultaneously by ICCS. Recent applications of the ICS and ICCS methods for characterizing the transport and clustering of GFP labeled alpha-actinin adhesion proteins in living fibroblasts will be presented. Image correlation studies which demonstrate simultaneous measurement of diffusing and flowing populations of alpha-actinin clusters, and correlated transport between the alpha-5 integrin and intracellular alpha-actinin in CHO fibroblasts at 37C will be shown. We will show spatially resolved vector maps of directed flow of proteins in living cells as measured using our new spatio-temporal ICS method.

11:40am **BI2-WeM11 Microspectroscopic Probing of Intracellular Structures by Observation of Infrared Linear Dichroism in Single Cells in a Micro-Fluidic Cuvette*, M. Schmidt,*** University of Maine*; M. Rumpler, N. Gierlinger,* Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Germany*; U. Schade,* BESSY GmbH, Germany*; T. Rogge,* Forschungszentrum Karlsruhe GmbH, Germany*; P. Fratzl,* Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Germany*; M. Grunze,* University of Maine and Universität Heidelberg, Germany

Cellular properties and functions are closely related to cell structure. Probing intracellular structures and their dynamic nature is essential for the understanding of the functional characteristics of cells. Infrared (IR) microspectroscopy is an attractive tool for the investigation of biological materials and systems.@footnote 1@ Combining@footnote 2@ this technique with polarization modulation@footnote 3,4@ (PM) and employing synchrotron IR radiation allows us to perform polarization-dependent measurements with high spatial and temporal resolution. Thus, we are able to measure IR linear dichroism (LD) and hence determine preferred molecular orientation of distinct biochemical species in individual cells. Ultimately, observing single living cells in their native environment seems desirable when studying cell structure and function. Therefore, we developed an IR cuvette which facilitates the investigation of individual cells in aqueous solution. This custom-built, demountable and temperature-controllable micro-fluidic cuvette was microfabricated in order to meet the requirements of low pathlength (8 µm) and low volume (1 µL). Our goal is to gain insights into the formation and organization of the cytoskeleton in the context of cell adhesion. Using substrates with well defined surface properties and geometries we seek to control and model cell adhesion. Importantly, IR LD serves as an intrinsic marker for the preferred molecular orientation of the fibrous cytoskeletal proteins. Introduction of external stimuli such as chemicals, mechanical stress and substrate surface variation can be used to study the dynamic response and structural changes inside the cells. @FootnoteText@ @footnote 1@H.Y.N. Holman et al., J. Biomed. Opt. 7, 417 (2002).@footnote 2@Y. Shigematsu et al., Rev. Sci. Instrum. 72, 3927 (2001).@footnote 3@L.A. Nafie and M. Diem, Appl. Spectrosc. 33, 130 (1979).@footnote 4@T. Buffeteau et al., J. Chim. Phys. 90, 1467 (1993).

Electronic Materials and Processing
Room 309 - Session EM+SS-WeM

Contacts to Organic and Molecular Devices

Moderator: Y. Roichman, Princeton University

8:20am **EM+SS-WeM1 Energy Level Alignment at Interfaces in Organic Semiconductor Devices*, K. Demirkan,*** *A. Mathew, S. Vaidyanathan, Z.I. Niazimbetova, H. Christian-Pandya, M.E. Galvin, R.L. Opila,* University of Delaware

Poly-phenylene vinylene based organic semiconductor polymers and oligomers were studied using X-ray Photoelectron Spectroscopy (XPS) and Ultraviolet Photoelectron spectroscopy (UPS). Valence bands and highest occupied molecular orbitals (HOMOs) (with respect to Fermi level) for these organic structures were determined. Due to the high electron withdrawing property of the oxadiazole moiety, polymers, which have a higher oxadiazole density, are found to have lower energy levels. Using optical absorbance spectra, the lowest unoccupied molecular orbitals (LUMO) for some of the organic semiconductor materials were estimated and the basic energy level diagrams were established with respect to the underlying electrode. The valence band spectra of the polymers spin coated on different substrates did not show any substantial variation except for shifts in the entire spectra. In the Mott-Schottky limit, the energy difference between the electrode Fermi level and the HOMO of the organic layer is expected to follow the work function of the electrode. The interface slope parameter, a measure of the change in HOMO-Fermi level difference as a function of electrode work function, was found to vary between 0.4 and 0.9. These values are intermediate to Mott-Schottky and Fermi level pinning. We will explain the interface slope parameter in light of the interfacial dipole and charge neutrality level at organic/metal interfaces.

8:40am **EM+SS-WeM2 Towards Molecular Electronic Circuitry: Selective Deposition of Metals on Patterned Self-Assembled Monolayer Surfaces***, C. Zhou, G. Nagy,* ***A.V. Walker,*** Washington University in St. Louis

We have developed a robust method by which to construct complex two- and three- dimensional structures based on controlling surface chemistry. This work has important applications in molecular and organic electronics, sensing, biotechnology, photonics and other technologies. Our method is extensible to many different types of materials, easily parallelized, affords precise nanoscale placement and is fully compatible with photolithographic fabrication processes. The method is based on the deposition of metals on UV-photopatterned self-assembled monolayers (SAMs). To demonstrate the method we have selectively vapor-deposited Mg on a patterned -CH@sub 3@/-COOH terminated alkanethiolate surface. The deposited metal penetrates through the -CH@sub 3@ SAM to the Au/S interface while reacting with the -COOH terminal group and accumulating on top of the other SAM.

9:00am **EM+SS-WeM3 Interface Disorder and Charge Injection into Organic Semiconductors*, M.A. Baldo,*** *B.N. Limketkai,* MIT **INVITED**

In this talk, we examine the effect of structural disorder at the injection interface on the current-voltage (IV) characteristics of organic semiconductors. We find that structural disorder at the injection interface creates energetic disorder, which in turn may dominate the IV characteristics of these materials. We will describe the effects of interfacial disorder on charge injection in several model systems: flat metal electrodes, rough metal electrodes, and highly conductive polymer electrodes. Disorder is most important at interfaces with relatively small energetic barriers between the metal and semiconductor.

9:40am **EM+SS-WeM5 Modelling Inhomogeneities of Organic Device Contacts: Organic Film Growth on Nanostructured Surfaces*, M.G. Ramsey,*** *B. Winter, S. Surnev, G. Koller, F.P. Netzer,* Karl-Franzens-University Graz, Austria

In this contribution the growth, geometric and electronic structure of sexiphenyl films grown on clean Cu(110) and mesoscopically patterned Cu(110)-(2x1)O will be presented. The results highlight the effects of the atomic and nanometric substrate structure on the growth and electronic level alignment of active organic films. Scanning tunnelling microscopy (STM) reveals that on the clean Cu the molecules align parallel to each other and are highly mobile in one surface direction. By monolayer coverages a complete layer forms reminiscent of a smectic liquid crystal phase. Despite the lack of strict long range order the molecules align in strings with a periodicity determined by intermolecular interactions, while the periodicity between the strings is determined by the substrate periodicity. In contrast when the substrate is covered with a half monolayer of oxygen the molecules appear not to wet the surface and, apart from at defects, are not visible in STM. On the mesoscopically patterned Cu(110)-(2x1)O (stripes of clean and oxygen covered surface with a periodicity of ~ 7 nm) the molecules first appear at the Cu-CuO boundaries and then grow preferentially on the clean Cu stripes. Growth and electronic structure on the three basic substrate situations are also followed by angle resolved ultraviolet photoemission spectroscopy (ARUPS). These results highlight the problems of imaging such wide band gap materials with STM and indicate that the 6P does in fact wet the Cu(110)-(2x1)O and that the visibility of the molecule is dependent on charge transfer states in the gap. These ARUPS results will also be discussed in terms of the electronic level alignment on inhomogeneous surfaces where large band offsets between molecules on different regions occur.

10:00am **EM+SS-WeM6 The Influence of Alkyl Side-chains and Charge-Transfer Complex Formation on Sexithiophene/Metal Interface Energetics***, **S. Duhm**, H. Glowatzki,* HU-Berlin, Germany*; R.L. Johnson,* Hamburg University, Germany*; J.P. Rabe, N. Koch,* HU-Berlin, Germany

The energy level alignment at metal/organic interfaces is a key issue for improved performance of novel organic (opto-) electronic devices. In certain cases, solution-based processing of organic materials (i.e., spin-coating, ink-jet printing) is preferred over vacuum sublimation. Frequently, alkyl side-chains are attached to the conjugated moieties for improved solubility. In order to investigate the influence of alkyl side-chain addition on interface energetics, we studied interfaces formed between the organic molecules sexithiophene (6T) and @alpha@,@omega@-dihexylsexithiophene (DH6T) and the metal surfaces Ag(111) and polycrystalline Au with ultraviolet photoelectron spectroscopy (UPS). Samples were prepared by sublimation of the organic substances on clean metal surfaces in ultrahigh vacuum. Interestingly, we observed significantly lower hole injection barriers (0.2 - 0.4 eV) for DH6T on the metal surfaces than for 6T. We propose that the mechanism responsible for our observations is closely related to the "electron push-back effect" at metal/organic interfaces. Furthermore, the influence of molecular orientation will be discussed. Additionally, we demonstrate that the hole injection barrier at interfaces between 6T (DH6T) and metals can be further reduced by the formation of charge transfer complexes comprising tetrafluoro-tetracyanoquinodimethane (F4-TCNQ).

10:20am **EM+SS-WeM7 Top-contact Junctions for Molecules Electronics: Nano-transfer Printing***, **K. Ojima**,* Osaka University, Japan*; K. Nakamatsu,* University of Hyogo, Japan*; Y. Otsuka, T. Matsumoto,* Osaka University, Japan*; S. Matsui,* University of Hyogo, Japan*; T. Kawai,* Osaka University, Japan

Recently, nanotransfer printing (nTP) attracts an attention as a method of producing the electrode. The electrode fabricated by nTP give the solutions for the problems of bottom contact-type electrode because electrodes are fabricated directly on the substrate after the deposition of molecules. In the previous reports, the nTP process needed chemical modification for the substrate in order to obtain well adhesiveness between the electrode and the substrate. This requirement has been serious limitation to fabricate molecular-scale devices. We have developed a nTP process for molecular devices without any modifications of substrate surfaces and evaluated the electrical properties of the electrodes fabricated by nTP. The use of the release agent enables us to print electrodes without any surface modification and heating the substrate. A test pattern of gold electrodes formed by the nTP on a DNA spread SiO2/Si substrate was examine by AFM. We found that the resistivity of a line of gold electrode is nearly equal to that of bulk gold. We also examined the electric contact between the electrodes and molecules using Kelvin force microscopy (KFM) under applying bias voltage to the electrode/molecules junctions. We will present the images of electric potential distribution for the junctions.

10:40am **EM+SS-WeM8 Orbital Alignment and Chemical Interaction at Macro-Molecular Contacts**, *M.M. Beerbom, B. Lagel, J.P. Magulick, A.J. Cascio,* ***R. Schlaf***, University of South Florida

Our experiments aim at the determination of the chemical and electronic structure of interfaces between macro-molecules and inorganic materials to determine charge injection barriers across the interfaces, the electronic structure of the highest occupied molecular orbitals (HOMO), and the chemical interaction between the materials in contact. Photoemission spectroscopy (PES) was used in combination with multi-step in-situ deposition of macro-molecular materials on inorganic substrates. PES characterization between deposition steps yields a sequence of spectra allowing the determination of the orbital line-up. Multi-step deposition was achieved using either a unique electrospray thin film deposition system, or a glove-box based deposition procedure. This allowed the fabrication of pure and non-contaminated interfaces suitable for PES measurements. Results from a series of experiments on poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV),@footnote 1@ ribonucleic acid (RNA@footnote 2@) and L-cysteine (amino acid)@footnote 3@ interfaces will be presented. The electronic and chemical structure of these interfaces will be discussed as well as the measurement technique. @FootnoteText@ @footnote 1@N. Dam, M.M. Beerbom, J.C. Braunagel and R. Schlaf: "Photoelectron Spectroscopic Investigation of In-Vacuum Prepared Luminescent Polymer Thin Films Directly From Solution", J. Appl. Phys. 97(pp.024909 (2005).@footnote 2@N. Dam, B.V. Doran, J.C. Braunagel and R. Schlaf: "Charge injection barriers at a ribonucleic acid/inorganic material contact determined by photoemission spectroscopy", J. Phys. Chem. 109(2), pp.748-756 (2005).@footnote 3@M.M. Beerbom, R. Gargagliano and R. Schlaf: "Determination of the Electronic Structure of Self-Assembled L-cysteine/Au Interfaces Using Photoemission Spectroscopy", Langmuir Articles ASAP), (2005).

11:00am **EM+SS-WeM9 Self-assembled Monolayers with Reactive Endgroups: Studies of Inorganic-Organic Interfaces and the Initiation of Top Contact Formation***, **A. Dube**, M. Sharma, A.S. Killampalli, J.R. Engstrom,* Cornell University

Self-assembled monolayers (SAMs) have attracted considerable interest over the past several years in the field of molecular electronics. In such applications two interfaces become important, and understanding the formation of both is critical to effectively making use of SAMs in these devices. While formation of the bottom contact is a well studied area, the formation of top contacts is an immature field. We have been examining the reactions of transition metal coordination complexes, such as Ti[N(CH@sub 3@)@sub 2@]@sub 4@ and Ta[N(CH@sub 3@)@sub 2@]@sub 5@, with SAMs possessing different head group chemistries [e.g., RSiCl@sub 3@ on SiO@sub 2@, R-(thiophene) on Au] and endgroup functionalities (e.g., -CH@sub 3@, -NH@sub 2@ and -OH) in order to develop an understanding of interface and contact formation. In this presentation we will highlight our most recent work that includes the self-assembly and reactions of functionalized molecular wires (thiophenes with conjugated ethynyl-phenylene backbones) adsorbed on Au using in situ angle resolved x-ray photoelectron spectroscopy (ARXPS). Here we find that the saturation density of the SAM increases from ~ 2.1 to 3.4 x 10@super 14@ molecules-cm@super -2@ as the length of the conjugated backbone is roughly doubled. More importantly, these layers, which possess an isopropylamine endgroup, react via ligand exchange with Ti[N(CH@sub 3@)@sub 2@]@sub 4@ even at -50 °C, forming a structure that has a Ti:SAM stoichiometry of ~ 1:2. ARXPS shows conclusively that these Ti coordination complexes bond with the SAMs exclusively at the isopropylamine group, and can seed additional deposition of the top contact. We will discuss the importance of these and other results concerning what they say about designing an effective means to make top contacts to molecular monolayer structures.

11:20am **EM+SS-WeM10 Observation of Interface Gap-State between Pentacene Molecules and Gold Metal by Scanning Tunneling Spectroscopy***, **Y.J. Song**, S.H. Kim, Y. Kuk, K. Lee, J. Yu,* Seoul National University, Korea

Pentacene has been studied widely as a candidate for an organic thin film transistor (OTFT) because of its high mobility, and easy processing on various substrates. It has been pointed out that interface states work as scattering centers and results in poorly reproduced potential barriers for various metal contacts in the transport measurement. In this work, we investigated the electronic structure of a single pentacene molecule adsorbed on Au(100) surface with one dimensional spatially-resolved scanning tunneling spectroscopy (1D SR-STS) to map position-dependent local density of states (LDOS).@footnote 1@ In the geometry of metal-pentacene-metal transport measurement with a single crystal or a thin film pentacene, the molecule is positioned as if it flat on the contact metal. This geometry can be achieved by adsorbing the molecule on a metal substrate. Au(100) surface was chosen since it offers both near-hexagonal and square symmetry, depending on a location of the (5x20) reconstruction. We measured SR-STS at various sites on the Au(100)-(5x20) surface. Unlike previously observed spectroscopy results on an insulator surface,@footnote 2@ two dominant features are clearly resolved in the HOMO-LUMO gap of the spectroscopy: 1) Au surface state peaks of which energy level is position independent, and 2) a HOMO derived gap state which depend on the registry of the pentacene molecule on the substrate.

We expect that these gap states work as a scattering center and change the barrier height between metal contact and organics in the transport measurement. A density functional theory (DFT) calculation confirms our observation. @FootnoteText@ @footnote 1@ Jhinhwan Lee, H. Kim, S.-J. Kahng, G. Kim, Y.-W. Son, J. Ihm, H. Kato, Z. W. Wang, T. Okazaki, H. Shinohara and Young Kuk, Nature (London) 415, 1005 (2002)@footnote 2@ Jascha Repp, Gerhard Meyer, Sladjana M. Stojkovic´, Andre´ Gourdon and Christian Joachim, Phys. Rev. Lett. 94, 026803 (2005)

Magnetic Interfaces and Nanostructures
Room 204 - Session MI-WeM
Magnetic Imaging and Spectroscopies

Moderator: M.E. Hawley, Los Alamos National Laboratory

9:00am **MI-WeM3 Development of Spin Resolved Photoemission Facility at the LLNL for the Electronic Structure Study of Actinides***, **J.G. Tobin**, S.-W. Yu,* Lawrence Livermore National Laboratory

We have developed a spin-resolved photoemission facility at the Lawrence Livermore National Laboratory (LLNL) to study the electronic structures of Actinides. Although great progress in the determination of the electronic structures of low-Z materials has been achieved through the use of angle-resolved photoemission in combination with synchrotron radiation, the electronic structures of Actinides are less easily accessible with this technique because the electronic structures are modified strongly by spin-orbit interaction. In addition, the radioactivity of Actinides prevents them from easy access for experiments. In this talk, we will address how such problems can be removed in the new facility and present preliminary data.

9:20am **MI-WeM4 A Comparative Study of the Magnetic Domain Structure of Mn Doped ITO Thin Films by Magnetic Force Microscopy***, **B.I. Kim**,* Boise State University, United Sates*; J.O. Holmes, M.R. Kongara, A. Punnoose,* Boise State University

Semiconducting Mn doped ITO thin films have been studied with different Mn doping levels using high resolution magnetic force microscopy (MFM) to understand the magnetic microstructure and uniformity of this room temperature ferromagnet. The film was prepared by sol-gel mediated spin coat technique, and the Co-coated tip (radius < 10 nm) was magnetized vertically using strong external magnetic field before the experiment. We collected four different MFM images (topographic image, magnetic force image, amplitude image and phase image) at the same time to obtain complementary information using ac mode MFM technique. Stable imaging condition could be achieved at distance 50 -100 nm between tip and sample. The magnetic domain structures observed in the ambient condition show thin labyrinthine features with 1-2 µm width for all Mn : ITO thin films regardless of the Mn doping level. MFM images also show that magnetic structures are connected differently depending on the Mn concentration. We could observe a reproducible image with small fine magnetic features with 10nm size for the repeated images, indicating the fine features comes from 8 nm ferromagnetic nanoparticles confirmed from TEM. The sectional profiles across magnetic domains indicate that the variation between positive and negative orientation for the 6% Mn doped samples is twice bigger than those at 9% and 3% doped magnetic films, consistent with an independent magnetization measurement. Comparison of magnetic phase images with those of longitudinal medium suggests that the magnetic moments of Mn : ITO orient vertically on the plane of film surfaces. The study indicates the amount of Mn doping influences the individual magnetic fine features as well as the connectivity of magnetic domains. These observed domain features suggest that magnetic structures on nano- and- macro- scale of Mn : ITO films are closely related to the amount of Mn doping and preparation condition.

9:40am **MI-WeM5 Spin Polarized Scanning Tunneling Spectroscopy of Nano-Scale Co Islands on Cu(111)***, **O. Pietzsch**,* University of Hamburg, Germany **INVITED**

At room temperature, triangular Co islands can be grown on Cu(111), protruding two atomic layers high above the Cu surface. Two different orientations of the triangles are observed, indicating a stacking fault with respect to the fcc stacking of the Cu substrate in one case. We have studied the structural, electronic, and magnetic properties of these islands with spin-averaged and spin-resolved scanning tunneling spectroscopy at low temperatures. Using a non-magnetic tunneling tip, we found the electronic properties of the differently oriented islands to be clearly inequivalent. In differential conductance (dI/dV) maps this leads to strong contrasts at the appropriate energies with signal asymmetries as high as 50 percent. Applying a magnetic tip, another source of contrast with similar strength becomes accessible, originating from the perpendicular magnetization of the islands.@footnote 1@ We discuss the Co spin polarization which is strongly energy dependent and repeatedly changes sign. Quite similar to the Cu substrate surface, the Co islands exhibit a standing wave pattern in the local density of states. In the case of Co, however, the responsible dispersive state is spin-polarized. This spin imbalance modifies the oscillation amplitude. A comparison of the Cu and Co patterns as a function of energy reveals yet another difference: while the Cu patterns indicate two-dimensional free-electron gas behavior, the Co patterns are affected by lateral electron confinement. We compare our observations with models based on an exact solution of the particle-in-a-triangular-box problem@footnote 2@ and a multiple scattering approach.@footnote 3@ @FootnoteText@ @footnote 1@ O. Pietzsch, A. Kubetzka, M. Bode, and R. Wiesendanger, Phys. Rev. Lett. 92, 057202 (2004).@footnote 2@ H.R. Krishnamurthy, H.S. Mani, and H.C. Verma, J. Phys. A: Math. Gen. 15, 2131 (1982).@footnote 3@ E.J. Heller, M.F. Crommie, C.P. Lutz, and D.M. Eigler, Nature 369, 464 (1994).

10:20am **MI-WeM7 Evolution of (Surface) Magnetic Moment and Magnetic Ordering Behavior in Epitaxial Transition Metal Films***, **K.R. Podolak**,* The Pennsylvania State University*; N. Janke-Gilman,* Latrobe University, Australia*; R.F. Willis,* The Pennsylvania State University

We report dichroism in angle-resolved x-ray photoemission with linearly polarized synchrotron radiation of the 3p core levels of the ferromagnetic elements Fe, Ni, Co, and their binary alloys.@footnote 1@ A systematic study of the spectral width (W) and the dichroism asymmetry amplitude (A) distinguishes the magnitudes of the elemental moments from the overall saturization magnetization. The Slater-Pauling curve is shown to be a plot of the stoichiometric mean saturization magnetization per atom. The spectral width (W) increases with increasing ferromagnetism. The dichroism asymmetry amplitude (A) senses the onset of disorder, instabilities, and changes in the magnetic anisotropy. These new measurements provide a new insight into the magnetic order in these thin film alloys and surface moment enhancement. @FootnoteText@ @footnote 1@ R.F. Willis and N. Janke-Gilman. Europhys. Lett., 69, 411 (2005).

10:40am **MI-WeM8 Spin-Resolved Core Level Photoemission of the Ni/Co/Cu(001) System Using Circularly Polarized X-Rays***, **T. Komesu**, G.D. Waddill,* University of Missouri-Rolla*; M.T. Butterfield, S.-W. Yu, J.G. Tobin,* Lawrence Livermore National Laboratory

We present spin-resolved 2p core level photoemission results for Co/Cu(001) and for Ni/Co/Cu(001). For the former we have collected the core level spectra by reversing the magnetization of the Co film emphasizing exchange effects in the spin-polarization as well as by reversing the helicity of the incident x-rays on an unmagnetized sample which isolates spin-orbit effects in the observed spin-polarization. For the exchange effects we observe strong spin polarization in the main peaks and a weaker spin polarization effect in the controversial satellite peak at ~4 eV higher binding energy than the main peaks. The spin-orbit spectrum shows strong spin-polarization throughout the spectral region that changes sign between the 2p3/2 and 2p1/2 peak consistent with its sensitivity to the core-hole spin-orbit coupling. Finally, we have studied the effects of charge transfer for the Ni/Co/Cu(001) system using spin-resolved photoemission where we see changes in the spin polarization of the main peaks and satellite features of both Ni and Co 2p core levels that can be understood in terms of charge transfer from the Co to the Ni as a function of Ni film thickness. These results establish that spin-resolved core level photoemission is a sensitive probe of electron correlation effects in thin magnetic films and surfaces. This work was performed under the auspices of the U.S. DOE by University of California Lawrence Livermore National Laboratory under contract W-7405-Eng-48.

11:00am **MI-WeM9 Medard Welch Award Lecture: Studies of Magnetic Materials and Nanostructures using Synchrotron Radiation Spectroscopy, Diffraction, and Holography***, **C. Fadley**[1],* University of California, Davis and LBNL, Berkeley **INVITED**

I will discuss several recent developments in studies of magnetic surfaces and magnetic nanostructures using synchrotron radiation, with special emphasis on work in the soft x-ray regime at the Berkeley Advanced Light Source. Instrumentation that has been developed to carry out multiple spectroscopies with varying degrees of surface sensitivity (photoemission, x-ray absorption, and x-ray emission) on a single sample will be introduced,

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[1] **Medard W. Welch Award Winner**

together with future prospects in photoemission based on higher-speed detection.@footnote 1@ Then a new standing wave-plus-wedge method for non-destructively studying buried interfaces in multilayer nanostructures will be considered.@footnote 2@ This method has permitted determining concentration and magnetization profiles through an Fe/Cr giant magnetoresistive interface,@footnote 2a@ as well as layer-specific densities of states in a magnetic tunnel junction consisting of FeCoB/FeCo/Al@sub 2@O@sub 3@.@footnote 2c@ This approach should also be useful in a variety of other interface studies,@footnote 2b@ with the use of soft x-ray detection permitting the study of more deeply buried interfaces.@footnote 2d@ Application of the multi-spectroscopy experimental system to the colossal magnetoresistive oxide materials La@sub 1-x@Sr@sub x@MnO@sub 3@ (x = 0.3, 0.4) will also be discussed, including the direct observation of charge localization on Mn in polaron formation@footnote 3a@ and surface stoichiometry characterization.@footnote 3b@ Finally, the prospects for element-specific determinations of local atomic and magnetic structure using photoelectron holography will be considered.@footnote 4@ Work supported by the Dept. of Energy, Basic Energy Sciences, Materials Science and Engineering Division, under Contract DE-AC03-76SF00098. @FootnoteText@ @Footnote 1@J.-M. Bussat, C.S. Fadley, B.A. Ludewigt, G.J. Meddeler, A. Nambu, M. Press, H. Spieler, B. Turko, M. West, G.J. Zizka, IEEE Transactions on Nuclear Science 51, 2341 (2004), with further details at: http://www.physics.ucdavis.edu/fadleygroup. @footnote 2a@S.-H. Yang, B.S. Mun, N. Mannella, S.-K. Kim, J.B. Kortright, J. Underwood, F. Salmassi, E. Arenholz, A. Young, Z. Hussain, M.A. Van Hove, and C.S. Fadley, J. Phys. Cond. Matt. 14, L406 (2002) @footnote 2b@S.-H. Yang, B.S. Mun, and C.S. Fadley, Synchrotron Radiation News 17 (3), 24 (2004) @footnote 2c@S.-H. Yang, B.S. Mun, et al., to be published @footnote 2d@M. Watanabe, B.C. Sell, et al. to be published. @footnote 3a@N. Mannella, A. Rosenhahn, C. H. Booth, S. Marchesini, B. S. Mun, S.-H. Yang, K. Ibrahim, Y. Tomioka, and C.S. Fadley, Phys. Rev. Lett. 92, 166401 (2004) @footnote 3b@N. Mannella et al., to be published. @footnote 4@C.S. Fadley, M.A. Van Hove, A. Kaduwela, S. Omori, L. Zhao, and S. Marchesini, J. Phys. Cond. Mat. 13, 10517 (2001)

Manufacturing Science and Technology
Room 207 - Session MS+MN+NS-WeM

Advanced Manufacturing for Nano-scale Devices & Systems

Moderators: L. Larson, SEMATECH, A. Testoni, Varian Semiconductor Equipment Associates

8:20am **MS+MN+NS-WeM1 Government Directions in Nanomanufacturing*, J.S. Murday,*** Naval Research Laboratory **INVITED**

As the U.S. National Nanotechnology Initiative heads into its second five year, there is increasing attention to the transfer of science discovery into innovative technology. The new NNI Strategic Plan identifies manufacturing of nanoscale materials, structures, devices, and systems as one of seven program areas for emphasis over the next five years. Both the Chemical and Semiconductor Industries have identified critical manufacturing issues at the nanoscale. This presentation will provide an assessment of the present state-of-art, the challenges facing nanomanufacturing, and the government efforts to address those challenges.

9:00am **MS+MN+NS-WeM3 Next Generation Semiconductor Devices based on Carbon Nanotubes*, T. Rueckes,*** Nantero, Inc. **INVITED**

Nantero is developing carbon nanotube-based nonvolatile Random Access Memory (NRAM@super TM@, a high density, high speed, low power universal memory. The target markets in aggregate exceed $100B in revenue per year. To support the development of NRAM@super TM@ Nantero has enabled a unique nanoelectronics platform that for the first time allows the use of carbon nanotubes in DUV production CMOS fabs. Single-walled carbon nanotubes have a combination of properties that make them highly valuable for use in electronics applications, such as higher electrical conductivity than copper, higher thermal conductivity than diamond, higher strength than steel, and molecular-scale size (diameter of 10Å, wall thickness of 1 carbon atom) combined with high chemical and thermal stability. However, there were substantial barriers to using this material in a mass production process: nanotubes could not be positioned reliably on wafers, they were available only with substantial particulates and contaminants and device properties were hard to control. Nantero has developed solutions to all of these problems which now allow carbon nanotubes to be used in production CMOS processes on established tool sets in existing semiconductor fabs. Nantero's carbon nanotube-enabled NRAM@super TM@can be used as an embedded memory within logic products such as microprocessors, ASICs, programmable logic or as a standalone memory that can replace multichip packages in cell phones and enable instant-on computers.

10:20am **MS+MN+NS-WeM7 Assembly Pathway to Nanotechnology: Meso to Micro to Nano*, J.R. Von Ehr,*** Zyvex Corporation **INVITED**

Zyvex is the first molecular nanotechnology company, with a vision of developing adaptable, affordable, molecularly precise manufacturing. This talk will show the progression from macroscopic manipulation, to meso-scale (millimeter), to micro-scale, and ultimately to nano-scale. Zyvex has several years of experience in building and selling nanomanipulation tools, as well as a number of microassembled MEMS products under development, including a miniature mass spectrometer. New work to be discussed is an approach to Atomically Precise Manufacturing, using UHV STM-mediated depassivation of silicon followed by repetitive cycles of Atomic Layer Deposition/Epitaxy to build 3D structures with atomic precision.

Nanometer-Scale Science and Technology
Room 210 - Session NS-WeM

Nanometer Scale Imaging

Moderator: R. Bennewitz, McGill University

8:20am **NS-WeM1 Atomic Scale Analysis of Dielectric Surfaces and Nanostructures*, M. Reichling,*** Universitaet Osnabrueck, Germany **INVITED**

Nanostructures involving dielectric materials play an increasingly important role in numerous fields of science and technology. Prominent examples are ultra-precision machined optical surfaces, high-k dielectrics and diamond in microelectronics, catalytic surfaces and insulating substrates for sensor applications and molecular electronics. Dynamic scanning force microscopy (SFM) operated in the so-called non-contact mode is the method of choice for an atomic scale characterisation of such structures. The method of dynamic SFM is introduced as the only analysis tool capable of atomic resolution imaging of insulating surfaces and nanostructures. The state of the art in highest resolution dynamic SFM on insulators and challenges for future developments are illustrated for examples from different fields of application. While a detailed interpretation and quantitative understanding of atomic contrast formation is demonstrated for fluoride surfaces, the formation and dynamics of surface defects is discussed for oxide surfaces.

9:00am **NS-WeM3 Bioelectromechanical Imaging by Scanning Probe Microscopy: Galvani's Experiment on the Nanoscale*, S.V. Kalinin,*** Oak Ridge National Laboratory*; B.J. Rodriguez,* North Carolina State University*; S. Jesse, A.P. Baddorf,* Oak Ridge National Laboratory*; A. Gruverman,* North Carolina State University

Coupling between electrical and mechanical behavior is a universal feature of biological systems. However, macroscopic studies are inherently limited by the complex structure of these materials. Here, we demonstrate a scanning probe microscopy (SPM) based approach for electromechanical imaging and spectroscopy of biological systems based on Piezoresponse Force Microscopy (PFM). Electromechanical imaging of tooth dentin and enamel has been performed using PFM with sub-10 nm resolution. Characteristic piezoelectric domain sizes and local protein fiber ordering in dentin have been determined. The shape of a single collagen fibril in enamel is visualized in real space and local electromechanical hysteresis loops are measured. We have also shown that the electromechanical response vector is related to the local molecular orientation and provides an approach for molecular orientation imaging in biological systems. This technique is further used to address several biological systems, including cartilage, antler, bone, and butterfly wing. This approach repeats Galvani's experiment on the nanoscale - 230 years later and with a million times higher resolution. The future opportunities of electromechanical SPM for characterization of complex biological systems are discussed. Research performed as a Eugene P. Wigner Fellow (SVK) at ORNL, managed by UT-Battelle, LLC under DOE contract DCE-AC05-00OR22725. AG acknowledges financial support of the National Science Foundation (Grant No. DMR02-35632).

9:20am **NS-WeM4 Bridge Enhanced Nanoscale Impedance Microscopy*, L.S.C. Pingree,* *M.C. Hersam,* Northwestern University

Bridge Enhanced Nanoscale Impedance Microscopy (BE-NIM) advances the ability to measure the impedance of individual nanoscale conductive pathways in a variety of materials. Similar to Nanoscale Impedance Microscopy (NIM),@footnote 1@ this technique concurrently monitors the magnitude and phase response of the current through a conductive AFM tip in response to an AC bias. By varying the frequency of the driving potential, the resistance and reactance of nanometer scale conductive pathways can be quantitatively determined. Previously, we have demonstrated the extreme accuracy of NIM on a variety of control systems, such as a set of gold nanowires connected to known impedances, resulting in concurrent current and phase images. In addition, we have performed NIM on 8 µm x 8 µm Organic Light-Emitting Diode (OLED) pixels, which exhibit enhanced negative capacitance.@footnote 2@ However, the effects of long-range electrostatic interactions impose a detection limit on NIM of ~1 pF. These interactions, or fringe capacitance, act as a capacitor in parallel with the sample/tip junction. BE-NIM minimizes the contribution of this capacitance by employing a LRC bridge that improves the detection limit to ~50 aF. This improved sensitivity has been demonstrated on metal-oxide-semiconductor capacitors ranging in size from 5 fF to 50 aF. The application of BE-NIM to other materials systems, such as carbon nanotube/polymer composites and sub-micron OLEDs, will also be discussed. @FootnoteText@ @footnote 1@ L. S. C. Pingree, et al., IEEE T. Nanotechnol., 4, 255 (2005).@footnote 2@ L. S. C. Pingree, et al., Appl. Phys. Lett., 86, 073509 (2005).

9:40am **NS-WeM5 Development of a Tunable Microwave Frequency Alternating Current Scanning Tunneling Microscope to Profile Dopant Density in Semiconductors*, A.M. Moore,*** The Pennsylvania State University*; B.A. Mantooth,* GeoCenters*; P.S. Weiss,* The Pennsylvania State University

We have built a scanning tunneling microscope (STM) capable of profiling dopants in semiconductor devices and test structures at sub-nanometer resolution. The alternating current signals, and thereby the dopant density and type, are obtained through a heterodyned signal. Two frequencies are applied to the STM tip and the nonlinearity of the tunnel junction mixes the frequencies, generating new signals including at the difference of the frequencies applied; this in combination with the DC bias yields information on the dopant density and type. This ultrahigh resolution (<1 nm) profiling tool enhances what is obtained through current metrology tools and will support semiconductor processing as the size scale of devices continues to decrease.

10:20am **NS-WeM7 Single-Electron Charging in InAs Quantum Dot Observed by NC-AFM*, P. Grutter,*** McGill University, Canada **INVITED**

In this paper, we present the first successful observation of single electron charging events in an individual InAs QD by spectroscopic measurement with a 4.5K vacuum non-contact AFM (NC-AFM). The main features of the experimental results agree with a simple theory based on the semiclassical theory of the Coulomb blockade effect.@footnote 1@ The sample structure consists of a two dimensional electron gas (2DEG) layer used as a back electrode. The uncapped InAs QD were grown on top of a InP spacer layer serving as a tunneling barrier. The resonant frequency shift and the dissipated energy of an oscillating AFM cantilever were measured as a function of the tip-back electrode voltage, and the resulting spectra show distinct jumps when the tip was positioned above a QD. The observed jumps in the frequency shift, with corresponding peaks in dissipation, are attributed to a single-electron tunneling between the dot and the back electrode governed by the Coulomb blockade effect, and are consistent with a model based on the free energy of the system. The observed phenomenon may be regarded as the force version of the Coulomb blockade effect. The peaks in dissipation are essentially due to a single electron back action effect on a micromechanical transducer. This NC-AFM based technique has several advantages: It does not need any leads to be attached to individual QD and is also much less invasive for the mesurement of quantum states in the QD because only weak, controllable coupling between the tip and the QD is required. @FootnoteText@ @footnote 1@ Stomp et al., Phys. Rev. Lett. 94, 056802 (2005).

11:00am **NS-WeM9 Development and Characterisation of Reference Materials for Nanotechnology: High Lateral Resolution Auger Electron Spectroscopy on Semiconductor Heterostructures***, J. Westermann,* ***U. Roll,*** Omicron NanoTechnology GmbH, Germany*; M. Senoner, W. Unger,* Federal Institute for Materials Research and Testing, BAM, Germany

Today, a broad variety of different techniques and instruments is used to characterise nanoscale materials. However, a comparison between results taken with different instruments is often difficult or impossible. To overcome this gap, the Federal Institute for Materials Research and Testing (BAM), the Physikalisch-Technische Bundesanstalt, ION-TOF GmbH and Omicron Nanotechnology GmbH have entered into a project to develop reference samples with nanoscale structures. We report on the characterisation of the first prototype of a semiconductor heterostructure with alternating AlGaAs and GaAs layers. The cross section of the epitaxially grown multilayer stack shows a variety of strips in the thickness range between 700nm and well below 10nm. The strip pattern includes strip gratings, isolated narrow strips and wide strips with step transitions. SEM and Auger measurements with highest lateral resolution (sub 10 nm) reveal the distribution of the various elements on the sample surface, and prove the quality of the sample preparation. We discuss the suitability of the sample to become a widely accepted, certified reference standard for lateral resolution in surface chemical analysis.

11:20am **NS-WeM10 STM and AFM Imaging with In-Situ Tip-Characterization*, C.J. Chen,*** *O. Pietzsch, D. Haude, R. Wiesendanger,* Hamburg University, Germany

The biggest unknown factor in STM and non-contact atomic-force microscopy (NC-AFM) experiments is tip electronic states. Experimental observations show that the STM and AFM images vary dramatically with change of tip structure, either intentionally, or spontaneously. Conceptually, tunneling is symmetric to tip and sample, and the STM and AFM images should be determined by a convolution of tip electronic states and sample electronic states. From the beginning of STM, various attempts to characterize the tip have been proposed and tried, most notably using FIM. However, the correlation between the FIM image of the tip and the tip electronic states relevant to STM and AFM imaging is still not clearly identified. For spin-polarized STM, the azimuthal dependence of spin polarization of tip electronic states often determines the images. Currently, there is no well-defined method to determine the azimuth of spin polarization. We present a new method for determining the tip electronic states and the azimuthal dependence of spin polarization of the tip by imaging the tip with well-understood samples. For general tip states, Si(111)7X7 is an ideal standard sample, because the dangling-bond states on the adatoms are well separated in space and the mean energy levels cover more than 1 eV across the Fermi level. For spin-polarized tips, the Fe monolayers on W(001) system provides a perfect standard sample, because of its well-known properties of providing different ferromagnetic orientations.@footnote 1,2@ Using tips characterized by standard samples to image unknown samples, image interpretation is becoming much more certain. Furthermore, through tip reconditioning and tip characterization, tip properties can be optimized to achieve maximum contrast. @FootnoteText@@footnote 1@M Bode, O Pietzsch, A Kubetzka, S Heinze and R Wiesendanger, PRL 86, 2142 (2001).@footnote 2@A Kubetzka, M Bode, O Pietzsch and R Wiesendanger, PRL 88, 057201 (2002).

11:40am **NS-WeM11 Towards the Fabrication of Ultra High Throughput Optical Fiber Probes*, B.C. Gibson,*** *S.T. Huntington,* University of Melbourne, Australia*; J. Canning, K. Lyytikainen,* University of Sydney, Australia*; J.D. Love,* Australian National University, Australia

Scanning near field optical microscopy (SNOM) has become an important characterization tool across all major disciplines of science. The ability to "cheat" the resolution limit in optical microscopy has enabled characterization of structures on a nanometer scale. At the heart of the technique is a metal coated scanning probe, which features a sub-wavelength aperture as a source or collector of light that explores the near-field of the sample surface. The key problem with this type of SNOM probe is the excessive loss that occurs, which effectively limits the sensitivity of the microscope. The high loss arises from attenuation through the sub-wavelength aperture, which is unavoidable. In addition, the high loss stems from an interaction with the metal coating at the tapered region of the tip. Preliminary theoretical models of tapered air-silica structured fibers suggest that this interaction with the metal may be reduced with the use of these fibers, along with a new type of fiber called a Fractal Fiber (special class of air-silica fiber), instead of using standard single-mode optical fibers. Tapering of these fibers has been performed using a custom-built CO@sub 2@ laser-based fiber pulling system to produce a prototype ultra high throughput optical probe. Initial optical throughput measurements have shown improved power levels to that of conventional SNOM probes. This suggests that the fiber design and fabrication is critical to the successful advancement of SNOM probes.

Plasma Science and Technology
Room 302 - Session PS+TF-WeM
Plasma Enhanced CVD and ALD

Moderator: M.C.M. Van De Sanden, Eindhoven University of Technology, The Netherlands

8:20am **PS+TF-WeM1 Developments of Plasma Copolymerization Technique for Deposition of low-k Films*, K. Kinoshita*,** *A. Nakano, N. Kunimi, M. Shimoyama, J. Kawahara,* Mirai-Aset, Japan*; O. Kiso, Y. Seino, Y. Takasu,* Mirai-Asrc, Aist, Japan*; M. Komatsu,* Sumitomo Chem., Japan*; K. Nakamura,* Chubu University, Japan*; T. Kikkawa,* Hiroshima Univ., Japan **INVITED**

We have proposed the strategic concept of scalable low-k materials for ULSIs which can be used over two or three technology nodes.@footnote 1@ The major challenge to realize this concept is controlling the dielectric constant and mechanical strength. A plasma copolymerization technique has been developed for this purpose.@footnote 2@ Basic film properties will be determined by the matrix monomer, and modified by copolymerization with modification monomers. A narrow-gap CCP was employed to generate uniform discharge over the 300 mm wafer. A divinylsiloxane-bis-benzocyclobutene (DVS-BCB) was chosen as a starting matrix monomer. The dielectric constant of the polymerized DVS-BCB film was 2.78. Electron density of this polymerization plasma was about 1.5E10 cm@super -3@ as measured by surface wave probe technique.@footnote 3@ Modification monomers were chosen from the view points of the reactivity, the estimated dielectric constant of the monomers, and the vapor pressure. To increase film modulus, phenyl compounds with unsaturated functional groups were introduced. The copolymerization ratio corresponded to the film modulus.@footnote 4@ To reduce dielectric constant, aliphatic compound was introduced. However, copolymerization with DVS-BCB at 400 °C could not reduce the dielectric constant due to decomposition of aliphatic components. A process of low temperature deposition followed by annealing was examined with 2-dimethylvinylsiloxane-tricyclodecane (2DMVS-TCD). A dielectric constant of 2.48 was obtained by deposition at 300 °C followed by annealing at 400 °C. This work was supported by NEDO. @FootnoteText@ @footnote 1@ T. Kikkawa, Ext. Abst. ADMETA 2003: Assian session, Tokyo, 1-2, (2003) 4,@footnote 2@ J. Kawahara, et al., Technical Dig. IEDM 2003, 6-2, (2003) 143,@footnote 3@ K. Nakamura, et al., Proc. Int. Symp. Dry Process 2004, Tokyo, P-29, (2004) 169,@footnote 4@ N. Kunimi, et al., Proc. IITC2004, San Francisco, 8.5, (2004) 134.

9:00am **PS+TF-WeM3 Amorphous Carbon Thin Films Deposition by Pulsed Substrate Biased PECVD using a CH@sub 4@-CO@sub 2@ Gas Mixture*, G. Gottardi*,** *N. Laidani, L. Calliari, M. Filippi,* ITC-Irst (Centro per la Ricerca Scientifica e Tecnologica), Italy*; R.S. Brusa, C. Macchi, S. Mariazzi,* Università di Trento, Italy*; M. Anderle,* ITC-Irst (Centro per la Ricerca Scientifica e Tecnologica), Italy

Various plasma-assisted deposition techniques and carbon bearing source materials have been investigated and can be used for the synthesis of a-C:H films. In particular, radio frequency (RF) plasma-enhanced chemical vapor deposition (PECVD) systems are the most common type employed, over a broad range of process conditions which are generally recognized to strongly influence the material properties. This research work intends to explore new perspectives in the hard carbon films production via PECVD, through the use of non-traditional gas precursors (CH@sub 4@-CO@sub 2@) and a voltage pulsing technology applied externally simultaneously to the film growth. The modulation of the substrate bias, when applied in a pulsed mode, provides in fact with more operative opportunities, broadening the process parameters set with respect to the conventional technology with a continuous bias and turning out to be much more effective in the densification and hardening of the material. A multi-technique approach has been used for a thorough characterization of the deposited films in order to highlight the effects of the gas precursor composition and of the ion bombardment due to the substrate bias on the chemical, structural and mechanical evolution of the material. In particular, the chemical composition and the structure were investigated with X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FT-IR) and electron energy loss spectroscopy (EELS). Positron annihilation spectroscopy (PAS) was performed for the detection of nano-scale open volume defects while nano-indentation and stylus profilometry techniques were used to evaluate the film hardness and internal stress.

9:20am **PS+TF-WeM4 Multi-hollow Plasma CVD Method for Depositing Cluster-free a-Si:H Films*, K. Koga*,** *K. Bando, M. Shiratani, Y. Watanabe,* Kyushu University, Japan

The three major limitations of a-Si:H solar cells are 1) light-induced degradation of cell efficiency, 2) a low deposition rate, and 3) a low cell efficiency. We have developed a multi-hollow plasma CVD method for depositing cluster-free a-Si:H films, since films incorporating less amount of a-Si:H nano-particles (hereafter refereed to as clusters) show better stability.@footnote 1@ For the method, powered and grounded electrode of 70 mm in diameter, which had 24 holes of 5 mm in diameter, were placed at a distance of 2 mm. Discharges were sustained in the holes using a VHF power source. A short gas residence time of ~ ms in the discharge regions suppressed growth of clusters and gas viscous force drives clusters toward the downstream region. Therefore, cluster-free a-Si:H films can be deposited on substrates set in the upstream region. Stability of the films against light soaking was evaluated with their defect density measured by ESR and a fill factor FF of a Schottky cell having a structure of Ni/a-Si:H/n type Si. The initial defect density of a film deposited at 0.12 nm/s is 3.5x10@super 15@cm@super -3@ and that after light soaking (7.5 hours under 2.4 SUN) is 3.7x10@super 15@cm@super -3@. The cell using a film deposited at 0.2 nm/s has a rather high stabilized FF of 0.50 and a small degradation ratio of 2.0 %. A higher deposition rate up to 0.66 nm/s can be obtained by utilizing a higher discharge power. Thus the multi-hollow plasma CVD method is effective in overcoming the three limitations for a-Si:H solar cells. @FootnoteText@ @footnote 1@K. Koga, N. Kaguchi, M. Shiratani and Y. Watanabe, J. Vac. Sci. Technol. A 22, (2004) 1536.

9:40am **PS+TF-WeM5 Proton/Deuteron Exchange in Functional Plasma Polymer Films (A Neutron and X-ray Reflectometry Study)**, *B.W. Muir,* ***C. Fong****, J. Oldham, P.G. Hartley, K. Mc Lean,* CSIRO, Australia*; A. Nelson, M. James,* Australian Nuclear Science and Technology Organisation

The plasma polymer (PP) deposition of chemically reactive monomers is frequently used to provide a chemical handle on inert surfaces. The characterization of the surface and internal structure of these thin films is critical in establishing their efficacy in technological applications. X-ray and neutron reflectometry are techniques that have become increasingly important in the characterisation of thin-film surfaces and interfaces; it now being possible to obtain angstrom precision depth profiles of a films composition. In this study, we have investigated the physico-chemical properties of allylamine plasma polymer thin films using X-ray and Neutron reflectometry in air and aqueous environments. Correlation of X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) data with X-ray and neutron reflectometry measurements on the PP film versus air, has allowed the stochiometric composition of the film to be obtained. The mass density was found to be 1.305 g/cm@super 3@ and film thickness 27.8 nm which correlated well with AFM measurements. Interestingly, when neutron reflectometry measurements are performed in D@sub 2@O we observe a significant increase in the scattering length density of the film from 2.033 e@super -6@ Å@super -2@ in air to 3.81 e@super -6@ Å@super -2@ in D@sub 2@O. By performing contrast experiments in mixtures of D@sub 2@O/H@sub 2@O we have found that a significant proportion of the protons within the film exchange with deutrons from solution. The films were found to contain approximately 3.3% water and 30% of the protons in the film are capable of exhanging, indicating significant functionality within the plasma polymer film. The study demonstrates that rich physicochemical information can be obtained on nano-scale thin plasma polymer films in different environments by combining a number of surface analytical techniques.

10:00am **PS+TF-WeM6 Anisotropic Deposition of Cu and Ru in Trenches by H-assisted Plasma CVD*, M. Shiratani*,** *T. Kaji, K. Koga,* Kyushu University, Japan

Previously we realized anisotropic deposition of Cu, for which Cu is filled preferentially from the bottom of trenches without being deposited on their sidewall, by H-assisted plasma CVD using Cu(HFAC)@sub 2@ as a source material.@footnote 1,2@ In this study, we have demonstrated anisotropic deposition of Cu from Cu(EDMDD)@sub 2@ and that of Ru from Ru(ACAC)@sub 3@. Ion irradiation to surface where deposition takes place, is the key to all of the anisotropic deposition processes, whereas deposition characteristics depend on materials. For Cu(EDMDD)@sub 2@ and Ru(ACAC)@sub 3@, the deposition rates on the bottom of trenches decrease with decreasing the trench width, while that for Cu(HFAC)@sub

2@ increases. These results suggest that anisotropic deposition by H-assisted plasma CVD using metal-complex has a potential to be applied to deposition processes of many kinds of metals, metal-oxide, and metal-carbide. We will compare deposition characteristics for Cu and Ru and discuss the deposition mechanisms. @FootnoteText@ @footnote 1@ K. Takenaka, et al., Pure. Appl. Chem. 77(2005)391.@footnote 2@ K. Takenaka, et al., J. Vac. Sci. Technol. A22(4) (2004) 1903.

10:20am **PS+TF-WeM7 Metal ALD Challenges in Microelectronics Fabrication*, K. Leeser,*** Novellus Systems Inc. **INVITED**

As device geometries continue to shrink, limitations are encountered with conventional thin film processing techniques. Some of these applications have begun the migration towards atomic layer deposition (ALD) as a means of addressing these limitations. Initial applications have focused on dielectric deposition for DRAM and gate stack, but the migration from fab R&D to production has been slow. Current trends indicate that ALD applications of metallic compounds and elemental metals will actually enter mainstream production at a faster rate than their dielectric counterparts with substantial evaluation activity already at the 45nm node, especially for backend metallization. However, metal ALD process technology, applications, integration, and hardware design are more difficult than those required for dielectric ALD. This presentation will highlight and discuss these critical challenges with emphasis on non-tungsten applications.

11:00am **PS+TF-WeM9 Plasma-assisted Atomic Layer Deposition of TiN Films at Low Substrate Temperatures*, W.M.M. Kessels,*** Eindhoven University of Technology, The Netherlands, Netherlands*; S.B.S. Heil, E. Langereis,* Eindhoven University of Technology, The Netherlands*; F. Roozeboom,* Philips Research Laboratories, The Netherlands*; M.C.M. Van De Sanden,* Eindhoven University of Technology, The Netherlands

Atomic layer deposition (ALD) is the method of choice for the deposition of ultrathin films with a high conformality and with precise thickness control. The extension of the technique with plasma processes (i.e., plasma-assisted ALD) opens up new routes in ALD that are difficult to attain by pure thermal ALD, as for example depositing high-quality films at low substrate temperatures. This is an important issue for metallic films such as TiN. High quality films can be deposited by ALD using the halide precursor TiCl@sub 4@ and NH@sub 3@ but this process is only applicable at temperatures of 350-400 °C. Lower deposition temperatures are, however, necessary for compatibility with some high-k oxides, processes involving Cu to avoid CuCl formation, and for improved barrier properties. Therefore we have developed a plasma-assisted ALD process of TiN using TiCl@sub 4@ dosing alternated with H@sub 2@-N@sub 2@ plasma exposure. The plasma is generated with a remote ICP plasma source and has been characterized by electrical probe measurements and optical emission spectroscopy. In situ spectroscopic ellipsometry has been used to monitor the growth rate per cycle (0.6 Å/cycle at 400 °C) and from a parameter study it has been proven that the surface reactions are self-limiting. TiN films have been deposited for substrate temperatures between 100-400 °C and the material properties have been analyzed by several diagnostics. Some key observations are that the deposition rate decreases and the Cl content and electrical resistivity increase with decreasing temperature. Nevertheless, the Cl content and resistivity remain relatively low for an ALD process. Furthermore, some plasma-related aspects for the ALD process will be discussed, such as facilitated initial growth on different substrates, surface modification of the underlying substrate (nitridation by N radicals), and the influence of wall-recombination of radicals in high-aspect ratio structures.

11:20am **PS+TF-WeM10 Characteristics of HfN deposited by using Remote Plasma Enhanced Atomic Layer Deposition Method*, K.W. Lee,*** *S.J. Han, G.J. Kim, W.H. Jeong, H.T. Jeon,* Hanyang University, Korea

Metal oxide films with high dielectric constants (high-k) have been studied recently to overcome the current disadvantages of SiO@sub2@ material. This high-k oxide material also need to apply new gate electrode because of the problems of polysilicon/high-k gate stacks such as poly-Si depletion effect, Fermi level pinning, surface phonon scattering, high threshold voltages and channel mobility degradation in real devices. Current polysilicon as a gate electrode results in poor transistor performance. Due to these problems new metal gate materials are needed to solve these problems because the metal/high-k gate stack is very effective in screening the phonon scattering and improves the channel mobility. And the use of metal gate electrode eliminates poly-Si depletion effect and Fermi level pinning. Among the many candidates the refractory metal nitrides such as titanium nitride (TiN) and tantalum nitride (TaN) are considered as the solutions to replace current poly-Si gate electrode. HfN exhibits various advantages such as thermal stability, midgap work function(4.65eV), and low lattice mismatch(1.13) with HfO@sub2@ gate dielectric and is considered as one of the most suitable candidates as gate electrode. In this work we studied this HfN material with remote plasma enhanced atomic layer deposition(RPEALD) method with tetrakis-ethylmethylamino-hafnium (TEMAH), Hf[N(CH@sub3@)C@sub2@H@sub5@]@sub4@ as a Hf precursor and NH@sub3@ plasma as a reactant gas. This HfN gate electrode was deposited on the HfO@sub2@ gate oxide. After deposition, the physical and chemical characteristics were evaluated, and MOS capacitors were fabricated with the HfN electrode to measure the electrical properties. The interfacial layers of deposited the HfN/HfO@sub2@ and the TiN/HfO@sub2@ stacks were investigated by high resolution transmission electron microscope (HRTEM).

11:40am **PS+TF-WeM11 Plasma-Enhanced Atomic Layer Deposition for Compositionally Controlled Metal Oxide Thin Films**, *R.M. Martin,* ***K.M. Cross,*** *J.P. Chang,* University of California, Los Angeles

The need to replace SiO@sub 2@ by a higher dielectric constant material in fabricating smaller and faster metal-oxide-semiconductor (MOS) transistors is well recognized by the National Technology Roadmap for Semiconductors. Atomic layer deposition emerges as a viable chemical processing technique to enable the deposition of ultra-thin and highly conformal thin films, and the use of plasma allows greater flexibility in designing doped or alloyed thin films with controlled compostition. In this work, we discuss the atomic layer deposition of HfO@sub 2@ and Hf@sub 1-x@Si@sub x@O@sub y@ using an alternating, cyclical sequence of hafnium terta-tert butoxide and tetra ethyl ortho silicate as the chemical precursors and oxygen radicals generated from an oxygen plasma as the oxidant. Optical emission spectroscopy (OES) was used to identify and quantify the gas phase atomic species. The thicknesses of the films scaled linearly with the number of deposition cycles as determined by both ellipsometry and x-ray photoelectron spectroscopy (XPS) measurements. Thin film composition of Hf@sub 1-x@Si@sub x@O@sub y@ can be varied and controlled by the chemical sequences, as verified by XPS compositional analysis. Atomic force microscopy (AFM) was used to determine surface roughness of the deposited films as a function of the deposition chemistry sequence and film thickness. MOS transistors were fabricated with the PEALD deposited films and capacitance-voltage (C-V) and current voltage (I-V) measurements showed that the PEALD HfO@sub 2@ films had a dielectric constant of 25 and an equivalent oxide thickness of 12.5-15 Å. Device results of Hf@sub 1-x@Si@sub x@O@sub y@ will be discussed as a function of the Si concentration and the resulting interfacial composition.

Plasma Science and Technology
Room 304 - Session PS-WeM

Advanced Gate Stack Fabrication

Moderator: S. Vitale, Texas Instruments

8:40am **PS-WeM2 Ta Based Metal Gate Etch for Dual Metal Gate CMOS Applications*, C.H. Huffman,*** *Z. Zhang,* Texas Instruments Assignee to SEMATECH*; S.C. Song,* SEMATECH

Although the ITRS states that low power applications may require high-k materials first, the high performance devices trend will soon require both high-k dielectrics and metal gate electrodes to remove polysilicon depletion effects. The selection of the metal gate material will be driven by the workfunction of the metal in order to control the threshold voltage of the transistors. Candidate metals should have a workfunction within 0.1v of the conduction band and the valance band edges for NMOS and PMOS respectively. The potential NMOS candidate metals are more reactive while the PMOS candidates are more noble like and this creates an etch challenge for dual metal CMOS integration. This paper will discuss the formation of dual metal gate CMOS structures using Ta based metal electrodes (TaN, TaSiN, TaCN). Affects of plasma parameters on the various metals will be discussed with respect to successful construction of dual metal gate CMOS. Differences in recipes for the various metals will be compared and contrasted with respect to successful construction of advanced metal gate electrodes. Included in the discussion will be potential process solutions for some of the common multiple material gate etch issues that occur. Optical endpoint control will be included for selected materials and process steps.

9:00am **PS-WeM3 Challenges in Plasma Processing for Advanced Gate Stack Fabrication***, **B.-W. Chan,*** Taiwan Semiconductor Manufacturing Corp., Taiwan*; Y.-H. Chiu,* Taiwan Semiconductor Manufacturing Corp.*; E. Luckowski, B. Goolsby, S. Rauf, P.J. Stout, B. White, P. Tobin,* Freescale Semiconductor*; H.-J. Tao, S.-M. Jang, M.-S. Liang,* Taiwan Semiconductor Manufacturing Corp. **INVITED**

High gate leakage current limits gate oxide thickness shrinkage in traditional SiO2 dielectrics. New gate stacks with novel material combinations are being investigated to reduce gate leakage while enhancing transistor performance. The combination of high K dielectrics and metal gates is a leading candidate for advanced CMOS gate materials but at the cost of increased complexity and greater challenge for the plasma processes that would be used to etch them. In this presentation, we will point out critical issues related to high K and metal gate etch and in particular dual metal gate fabrication. Examples of how simulation is being used to aid advanced gate etch development will also be presented. A specific focus of the talk will be gate trim process and resultant accurate critical dimension (CD) control and meeting CD control metrics required for beyond 65nm transistor fabrication.

9:40am **PS-WeM5 Challenges in Plasma Etching of Metal Gate Stacks***, **A. Le Gouil,*** STMICROELECTRONICS*; E. Richard, T. Chevolleau, G. Cunge, O. Joubert, L. Vallier,* LTM (CNRS), France

The rapid downscaling of metal-oxide-semiconductor transistors imposes the introduction of metal gates electrodes and high k gate dielectrics. Hence the patterning of a typical gate stack (Si/metal/high-k) requires the development of new etching processes. In this work the metal gate etching process is developed with both poly-Si/TiN and poly-Si/TaN stack for the gate electrode and HfO@sub2@ or HfSiO (3.5 nm thick) as the gate dielectric. First, the silicon part of the gate is etched using a standard HBr/Cl@sub2@ silicon gate etching process, which is followed by the metal etching step. By comparison with classical silicon etch processes two main issues are identified during the etching of the metal gate stack. First, when silicon etching stops on a metal instead of a SiO@sub2@ layer, a slope is observed at the bottom of the silicon etch profile. This difference is attributed to charging effect: charge accumulation on the insulator gate oxide deviate the ions towards the bottom of the gate (thus eliminating the gate foot), while this does not occur on a conductive metallic layer. Second, in the HBr-rich chemistry that is needed to etch the metal layer selectively towards the gate dielectric, a strong slope is systematically observed in the metal etch profile. This slope is attributed to the continuous increase of the mask dimension during the etching process due to the redeposition of precursors on the mask and feature sidewalls. We will show that these precursors originates from the SiOCl coating formed on the reactor walls during the silicon etching process, and which is subsequently sputtered during the metal etching step. This is a serious issue for critical dimension control in metal gate etching processes, and potential strategies to minimize it will be investigated.

10:00am **PS-WeM6 Investigation of Fluorocarbon Polymer Formation in Polysilicon Etching on Metal Gate***, **E. Luckowski,*** Freescale Semiconductor, Inc.*; B.W. Chan,* TSMC*; S. Rauf, A. Martinez,* Freescale Semiconductor, Inc.

It is well known that control of critical dimension and profile for ULSI devices with conventional polysilicon gates below the 90-nm technology node requires a detailed understanding of chemical etching and by-product deposition mechanisms in a plasma system. Carbon-containing feedstock gases such as CF4 are typically used in mixtures of Cl2, HBr, and/or SF6 to achieve a balance between deposition and etching required for profile control that also meet selectivity requirements for thin dielectric layers in MOSFET devices. Impact of chamber walls and contribution of species from masking materials can play an important role in the overall balance, as well as other additives such as O2 and N2. For advanced gate stacks, as conventional polysilicon gates are being replaced by metal gates to overcome polysilicon depletion effects, the impact of these various mechanisms on metal gate patterning must also be considered. In this work, we investigated the impact of polymer formation in polysilicon etch processes on the profile of polysilicon/transition metal gate stacks on high-K dielectrics. For fluorocarbon etching in particular, the C/F ratio has been found to strongly impact the final profile of polysilicon/metal gate stacks. OES and in-situ reflectometry were used to characterize composition and changes in the plasma conditions, while polymer formation and etch rate were characterized by SEM/TEM. Plasma modeling was also done using a 2D integrated equipment-feature scale model to improve understanding of the interaction between polysilicon and metal gate etch processes.

10:20am **PS-WeM7 Ion-Enhanced Plasma Etching of Metal Oxides in Chlorine Based Plasma***, **R.M. Martin,*** University of California, Los Angeles*; H.O. Blom,* Uppsala University, Sweden*; M. Sawkar, J.P. Chang,* University of California, Los Angeles

The development of plasma etching chemistries is necessary to pattern new gate dielectric materials, such as hafnium based oxides, for sub-65nm complementary metal oxide semiconductor (CMOS) devices. An electron cyclotron resonance high density plasma reactor is used in this work to study the etching of metal oxides and their corresponding metals in chlorine based chemistries. The plasma density, electron temperature, and gas phase species are characterized by a Langmuir probe, an optical emission spectrometer, and a quadrupole mass spectrometer. The etching of Al@sub 2@O@sub 3@, SiO@sub 2@, and HfO@sub 2@ was first studied in Cl@sub 2@ and BCl@sub 3@ plasmas, to allow for studies of the etching of hafnium aluminate, HfAl@sub x@O@sub y@, and hafnium silicate, HfSi@sub x@O@sub y@, with well controlled and varying compositions of Al and Si in HfO@sub 2@. The dominant etch products of Al and Hf metals in Cl@sub 2@ and BCl@sub 3@ plasmas were metal chlorides and metal boron-oxy-chlorides, respectively. These results enabled the assessment of the effect of metal-oxygen bond strength on the surface etching reactions, as well as the oxygen removal mechanism in the etching of metal oxides. The etch rates of hafnium aluminates were found to increase with the square root of ion energy, and the surface chlorination was enhanced with increasing ion energy, demonstrating that the etching reaction is limited by the momentum transfer from the ions to the film surface. The etching selectivity of HfAl@sub x@O@sub y@ and HfSi@sub x@O@sub y@ to Si in Cl@sub 2@ and BCl@sub 3@ plasmas will be presented, with a focus on the effect of increasing concentrations of Al and Si, and how the etch rates compare to the etching of Al@sub 2@O@sub 3@, SiO@sub 2@, and HfO@sub 2@ individually. Finally, the application of a generalized model, developed for the etching of ZrO@sub 2@ and HfO@sub 2@, to the etching of Hf aluminates and silicates in chlorine based plasmas will be discussed.

10:40am **PS-WeM8 ICP Etching of p-type Conducting Materials with High Work Function for CMOS Application***, W.S. Hwang, Y.Q. Wang,* National University of Singapore*; **W.J. Yoo**,* National University of Singapore, singapore*; V.N. Bliznetsov,* Institute of Microelectronics, Singapore

As metal electrode / high-k dielectric gate stacks are expected to be integrated for future complementary metal oxide semiconductor (CMOS) device process, extensive research on new conducting electrodes as a replacement for poly-Si is currently underway. Many candidate materials have already been identified as potential n-type conducting materials in the work function range of 4.0-4.5 eV. However, only a few conducting materials have high work functions above 5.0 eV to replace p-type poly-Si, and thus IrO@sub 2@, Ir, Ni, and Pt which meet this requirement are receiving significant attention as candidates of p-type conducting materials. Plasma etching of these materials is one of the most challenging issues in the integration of advanced CMOS gate stacks because of their chemically inert property. In this work, the etching properties of the p-type conductors / high-k gate stacks are investigated in SF@sub 6@ / Cl@sub 2@ / O@sub 2@ using inductively coupled plasma (ICP). Gas composition and plasma parameters of pressure, source power and bias power were changed to understand the etching mechanisms. The linear dependence of etch rates on the square root of bias voltages obtained from most of the above p-type conducting films indicated the dominance of ion induced etch mechanism in both SF@sub 6@ and Cl@sub 2@ etching. The effect of byproducts generated during etching on surface properties showed two different trends, depending on which type of by-product formation is predominant: volatile or nonvolatile. This phenomenon was well explained by evaporation temperature and Gibbs free energy of formation of byproducts in SF@sub 6@ and Cl@sub 2@. X-ray photoelectron spectroscopy (XPS) also revealed that more residues remain after the Cl@sub 2@ etching than the SF@sub 6@ etching. Using the optical emission of fluorines and other halogenated compounds, we were able to control the etch endpoints from the gate stack using p-type conducting materials.

11:00am **PS-WeM9 Damage-free MOS Gate Electrode Patterning on Thin HfSiON Film Using a Neutral Beam Etching***, **S. Noda**, T. Ozaki, S. Samukawa,* Tohoku University, Japan

We have already reported that our newly developed neutral beam could realize highly anisotropic gate electrode patterning on thin SiO@sub 2@ film with reasonable etching rate and etching selectivity.@footnote 1@ In this paper, radiation damages during the gate electrode patterning on thin HfSiON gate dielectric films (2nm) were investigated in our system. By changing the beam acceleration method (DC or RF voltages) in the neutral beam source, the beam flux and its composition (ratio between neutral and charged particles) could be controlled on the surface. Then, the leakage current of gate dielectric film was measured with antenna MOS capacitors. Although the gate leakage currents of the MOS capacitors measured just after the etching of poly-Si electrodes slightly increased in any conditions, its values were sufficiently lower (less than 1/10) than that in a conventional plasma etching. Since the leakage current increased according to over etching time, it was understood that a little degradation was caused by small stress current through the thin gate dielectric films due to the residual charges even during the neutral beam etching process. However, the residual charge current was extremely low and degradation of the gate dielectrics was negligibly small even if annealing was not performed in the neutral beam process. @FootnoteText@ @footnote 1@S. Noda et al., JVST A22,1506 (2004).

11:20am **PS-WeM10 Evaluation of Several Plasma Etching and Boron Cleaning Processes for Hafnium Oxide Thin Films on Silicon**, ***C. Wang***, *V.M. Donnelly,* University of Houston

At present, BCl@sub 3@-containing plasmas are commonly used to etch high dielectric constant ("high-k") materials such as HfO@sub 2@ and aluminum oxide. However, a boron residue is left on underlying surfaces during the overetch period. Boron is a p-type dopant; its presence is undesirable in subsequent processing. Previously, we reported that pure H@sub 2@ plasmas were effective in removing B from Si surfaces after HfO@sub 2@/Si and Al-oxide/Si samples were overetched in high density BCl@sub 3@ plasmas for 60 s. The underlying Si substrate, however, was etched about 15 nm. Here we report that dilute H@sub 2@/Ar plasmas (1 to 5% of H@sub 2@) are also effective in removal B, but in a more controlled fashion, such that the etching of the Si substrate can be minimized. After 60 s overetch in BCl@sub 3@ plasmas, HfO@sub 2@ samples were transferred under vacuum to an ultrahigh vacuum (UHV) for X-ray photoelectron spectroscopy surface analysis. B deposited during BCl@sub 3@ plasma etching was removed from the reactor walls in a pure H@sub 2@ plasma, and the samples were then returned to the plasma chamber and exposed to a dilute H@sub 2@/Ar cleaning plasma, and then re-examined by XPS. Under the best conditions (1% H@sub 2@/Ar plasma), > 90% of B was removed from Si in 20 s, while etching away

11:40am **PS-WeM11 Damage-free Ultrathin Oxynitride Films Formed Using Pulse-Time-Modulated Nitrogen Plasma**, ***S. Fukuda***, *C. Taguchi, Y. Kato, Y. Ishikawa, S. Noda, S. Samukawa,* Tohoku University, Japan

Ultra thin Si oxynitride (SiO@sub x@N@sub y@) films have been identified as leading candidates to replace conventional SiO@sub 2@ gate dielectrics for present and future ultra large-scale integrated circuits. Remote plasma processes for top surface nitridation of thermally grown oxides have been developed and applied in complementary MOS device applications. However, it is much difficult to control the concentration and position of nitrogen in ultrathin Si oxynitride film by using plasma processing and there are many serious problems, such as plasma radiation damage and increases in interface state density due to N penetrating the SiO@sub 2@-Si interface. To overcome these problems, we have already proposed pulse-time-modulated (TM) plasma nitridation.@footnote 1@ The pulsed nitrogen plasma makes it possible to restrain injection of higher energy particles from plasma into the silicon dioxide film. Then, the concentration and position of nitrogen in ultrathin Si oxynitride film could be controlled by changing the pulse-on time in the TM N@sub 2@ plasma. Additionally, the TM plasma could drastically reduce the UV and VUV photon radiation damages to Si oxynitride film, because of low electron energy during pulse-off time in the TM plasma. As a result, by using the TM plasma nitridation, NBTI characteristics were about 200 % improved at the maximum. TM plasma is very promising candidate as the damage-free nitridation method for SiO@sub 2@ and high-k films. @FootnoteText@ @footnote 1@ S. Samukawa, Y. Minemura, and S. Fukuda, Jpn. J. Appl. Phys. Vol. 42 (2003) pp. L795-L797.

Surface Science
Room 202 - Session SS+EM-WeM
Self-Assembled Monolayers

Moderator: P.S. Weiss, The Pennsylvania State University

8:20am **SS+EM-WeM1 Investigation of Mixed Fluorocarbon/Hydrocarbon Self-Assembled Monolayers on Au by Reactive Ion Scattering Spectrometry**, ***X. Yang***, University of Arizona*; S. Ravindran,* University of Texas*; A. Graham, K. Nebesny,* University of Arizona*; T.R. Lee,* University of Houston*; N.R. Armstrong, V.H. Wysocki,* University of Arizona

A series of mixed self-assembled monolayers (SAMs) of CF@sub 3@CF@sub 2@(CH@sub 2@)@sub 14@SH (C16F2) and CH@sub 3@(CH@sub 2@)@sub 15@SH (C16) were prepared on polycrystalline gold. Surface composition and crystallinity were first examined by XPS, FT-RAIRS and contact angle. Homogeneously mixed and well-ordered surfaces were formed. Results showed that surface composition followed solution composition uniformly. Reactive Ion Scattering Spectrometry (RISS) utilizing low-energy (<100eV) ion-surface collisions was used to investigate the mixture monolayers. Experiments are carried out in a tandem quadruple mass spectrometer. Precursor ions selected by the first quadrupole collide onto the surfaces at given collision energies. Neutralization and fragmentation of projectiles, ion-surface reaction and sputtering of surface species occur upon collision of the projectile ions with the surface. Product ions are extracted and analyzed by the second quadrupole. Benzene, tungsten hexcarbonyl and d4-pyrazine positive radical ions were used as projectile ions. As C16F2 concentration increases on the surface, projectile neutralization decreases, the amount of methyl/hydrogen abstraction decreases non-linearly, and linear increases of translational to internal energy conversion upon collision of either benzene or tungsten hexcarbonyl are shown. RISS shows high sensitivity to composition and homogeneity of surfaces.

8:40am **SS+EM-WeM2 Surface Bonding and Dynamical Behavior of CH@sub 3@SH on Au(111)**, ***P. Maksymovych***, University of Pittsburgh*; D.C. Sorescu,* U.S. Department of Energy*; D.B. Dougherty, J.T. Yates, Jr.,* University of Pittsburgh

Alkanethiols are often used for the growth of self-assembled monolayers, which are ordered 2-D molecular films covalently bonded to a substrate, typically a gold surface. The bonding of alkanethiols to gold has remained a controversial issue. In particular, the bonding of the undissociated alkanethiols has not been addressed at the atomic scale so far. We have studied adsorption and surface chemistry of the smallest alkanethiol, CH@sub 3@SH, on the Au(111) surface using the Scanning Tunneling Microscopy (STM) at 5K and Density Functional Theory (DFT). It has been established that CH@sub 3@SH adsorbs and desorbs without dissociation. Using the STM, it was found that CH@sub 3@SH adsorbs on top of an Au atom on the defect-free surface, and undergoes hindered rotation at 5K. The barrier to rotation obtained by DFT calculations is ~0.1 kcal*mol@super -@@super 1@. The STM image of the rotating molecule has a shape of a flower with six petals. The pattern suggests that the potential minima directions occur for the rotating molecule at the six hollow sites surrounding the atop adsorption site. Furthermore, selective site occupation was observed on the length-scale of the herringbone reconstruction of the Au(111) surface. At very low coverage, the CH@sub 3@SH molecule was found to preferentially adsorb on the intrinsic defective sites on the surface, such as the herringbone "elbows" and random atomic step sites. At higher coverage preferential adsorption occured on the fcc-stacked regions of the herringbone reconstruction. The latter is explained by the variation of the surface stress across the Au(111) surface due to the herringbone reconstruction, which causes the mobile CH@sub 3@SH molecules to select the most exothermic adsorption sites available at various coverages. We thank the W. M. Keck Foundation and NEDO (Japan) for financial support of this work.

9:00am **SS+EM-WeM3 Diffusion and Aggregation of Thiol-Linked Organic Molecules on a Cu(111) Surface**, ***K.L. Wong***, *K.-Y. Kwon, X. Lin, L. Bartels,* University of California at Riverside

We have investigated the adsorption geometry and the detailed surface dynamic behavior of benzenethiol (BT) molecules on a Cu(111) surface at low temperatures (50-60K). We chose BT as a model system, because it contains both the aromatic moiety and the thiol linker common in molectronic molecules, yet it is sufficiently small to be treated at high resolution experimentally and theoretically. The BT molecule adsorbs onto Cu(111) in two types of adsorption sites. In both cases the sulphur atom is believed to be adsorbed near the fcc hollow site while the benzene group is located near parallel to the surface. The more stable adsorption configuration (I) have the benzene ring centered near an hcp hollow site while the less stable adsorption configuration (II) have the benzene ring centered near an on-top site. The molecule can change adsorption configurations by rotation around the sulphur atom. Rotation from (II) to (I) occurs more rapidly than in the opposite direction. In addition to rotations the molecule can diffuse to nearby adsorption site. The sulphur atom jumps to one of six nearby adsorption sites along the high symmetry axis of Cu(111)while the orientation of the molecule with respect to the substrate remains the same. The rate of rotations and translations has been measured at different temperatures in the range 50-60K. An Arrhenius fit to the measured data yields rotations and diffusion barriers of 120meV, 130meV and 150meV respectively. DFT calculations show good agreement with the STM data. At higher coverages the adsorbed BT molecules from stable aggregates. No stable aggregates larger than 7 molecules were found, instead the density of evenly distributed 7-molecule aggregates increases with the coverage. Abundance histograms of aggregates with different sizes and configurations reveal a delicate balance between molecule-substrate and molecule-molecule interactions.

9:20am **SS+EM-WeM4 Tunneling Spectroscopy of Self-Assembled Monolayers of 1-adamantanethiolate on Single Crystal Metallic Substrates***, **A.R. Kurland**, A.A. Dameron, P. Han, S.U. Nanayakkara, P.S. Weiss,* The Pennsylvania State University

We measure local barrier height and differential conductance using ultrahigh vacuum scanning tunneling microscopy (STM) at 4 K to investigate the work function and local density of states, respectively, of individual adamantanethiolate molecules on a range of single crystal metallic substrates. These techniques allow us to probe specific electronic characteristics while simultaneously resolving the molecular lattice of the adamantanethiolate monolayers. Previously, we have shown that adamantanethiolate molecules form well-ordered hexagonally close-packed monolayers on the Au{111} surface. The complex and highly symmetric cage structure of adamantanethiolate results in weaker intermolecular interactions than those of alkanethiolate self-assembled monolayers. Taking advantage of these properties, we have implemented adamantanethiolate molecules in thin-film molecular lattices and as nanolithography patterning inks. We aim to exploit and to incorporate the unique physical and electronic interactions of adsorbed adamantanethiolate to understand and to tailor self-assembled nanostructures.

9:40am **SS+EM-WeM5 Interaction Pathways of Vapor Deposited Metal Atoms with Self-Assembled Monolayers***, **D. Allara**, N. Winograd,* Pennsylvania State University*; A.V. Walker,* Washington University*; T. Tighe, T. Daniel, O. Cabarcos, S. Uppili,* Pennsylvania State University **INVITED**

With rapid progress being made in the fabrication and testing of molecule-based electronic devices in the past several years one of the critical issues that has arisen is the character of the metal-molecule interfaces and interphases of vapor-deposited top contact device structures. Results will be discussed that show a broad strategy for developing correlations between the interactions of a wide variety of metals with a range of alkanethiolate/Au{111} self-assembled monolayers (SAMs) carrying varied terminal groups. The metals include inert coinage metals, one-electron donor alkali metal and aggressively reactive metals such as Ti. The SAMs range from those with hydrocarbon surface character to others with high electron acceptor character (-NO@sub 2@, C=N, C=O moieties) and including "solvating" types of groups such as -OCH3. The use of 4-5 different in-situ surface characterization tools augmented by DFT calculations aids greatly in achieving incisive information ranging from metal atom surface scattering to the evolution of the metal-molecule interface chemistry and the metal film morphology. Details include the distribution of metal and reaction products throughout the SAM structure, both laterally and extending to the substrate interface. Coupling this information with the character of the SAM/base electrode interface can provide critical information to aid fundamental interpretations of device behavior.

10:20am **SS+EM-WeM7 Replicative Generation of Electrode Structures by SAM-templated Electrometallization***, I. Thom, G. Haehner, **M. Buck**,* University of StAndrews, UK

Self-assembled monolayers (SAMs) of thiols provide a convenient way to modify electrode surfaces and, thus, to control charge transfer at an electrochemical interface. Adjustment of electrode properties from conducting to blocking is achieved by variation of the SAM forming molecules. Since a variety of methods is available to pattern thiol monolayers, this type of SAM can serve as templates to confine electrochemical processes, e.g. metal deposition. However, in addition to the control of charge transfer, SAMs serve also to control adhesion between deposit and electrode and, therefore, make the generation of metal structures by electrochemical deposition and subsequent transfer to a different substrate possible. Copper structures were produced by electrochemical deposition onto SAM-modified polycrystalline gold electrodes. Selective metal deposition was achieved by use of thiols which differ in their electrochemical blocking properties, namely hexadecane thiol and @omega@-(4'-methyl-biphenyl-4-yl)-methanethiol. After deposition the metal patterns were easily transferred to an insulating substrate by glueing. Characterization of the transferred structures with atomic force microscopy shows that the flatness of the metal surface is essentially determined by the initial SAM carrying substrate electrode. Since the thiol pattern on the substrate electrode remains intact, it can be repetitively used. Therefore, the process allows an easy and fast fabrication of high quality electrode patterns.

10:40am **SS+EM-WeM8 Alkylidyne Self-Assembled Monolayers on Pt(111): A Novel System for Molecular Electronics Applications***, **M. Yang**, A.R. Laracuente, L.J. Whitman,* Naval Research Laboratory

Although many alkanethiols form well-understood self-assembled monolayers (SAMs) on gold, such systems are of limited utility for molecular electronics applications given the incompatibility of gold with conventional silicon devices. Moreover, it is now widely recognized that the gold-sulfur bond inhibits electrical transport between the substrate and the bound organic molecules. Because of these issues, there has been recent interest in more compatible metals such as Pd and Pt, along with non-thiol bonding schemes for organic molecules. We are developing a new type of SAM/metal system based on direct carbon-to-metal bonding. When 1-hexene (C@sub6@H@sub14@) is vapor-deposited on clean Pt(111) in ultra-high vacuum, it converts into hexylidyne (C@sub6@H@sub11@) to form a self-assembled monolayer (SAM) with an upright geometry. Scanning tunneling microscopy studies show that the hexylidyne SAM on Pt(111) is a commensurate (3x3) overlayer. We have also investigated the influences of pressure, temperature, and coadsorbed hydrogen on the formation of the alkylidyne SAMs. Given that many of the organic molecules of potential use for current transport are alkanes and perylenes, direct carbon-metal bonding may provide the most desirable metal-molecule junction. Therefore, we believe this system has significant potential for developing molecular electronic devices.

11:00am **SS+EM-WeM9 Vertically Aligned Chromophoric Molecular Assemblies on a Si Surface***, **G.G. Jernigan**, M.F. Pepitone, J.S. Melinger, O.-K. Kim,* US Naval Research Laboratory

Strong motivation for the development of molecular devices is the ability to synthetically create a molecule with desired optical and electronic properties through the linkage of different chemical moieties. The challenge remains, however, to integrate such a molecule with a physical device. Molecules can take various physical conformations and can interact with nearby molecules or surfaces resulting in a loss of optical and electronic properties. We have developed a method for encapsulating a 4-[4-(Dimethylamino) styryl]-1-docosylpyridinium bromide (DASP) chromophore in a helical amylose sheath to produce a supramolecular assembly as a molecular device. The benefits of the supramolecular assembly formation are attributed to the ability of the amylose to rigidify the conformation of the DASP molecule, to individually isolate DASP molecules, and to prevent the DASP molecules from interacting with other DASP molecules to form aggregates. When DASP forms aggregates, the fluorescence is quenched, but when DASP is encapsulated by amylose, the fluorescence intensity is maximized. We report that when the supramolecular assemblies are self-assembled onto a Si surface that DASP emits a strong fluorescence with a spectrum that is similar to that found in solution. More importantly, AFM images show that the assemblies vertically self align at near monolayer coverage on the Si surface. We have subsequently linked a viologen species (electron acceptor) to the DASP (electron donor) through various hydrocarbon chain spacers resulting in distant-dependent electron transfer. We report this system as the basis for a molecular photodiode.

11:20am **SS+EM-WeM10 Laser Activation-Modification of Surfaces***, G. Jiang, M.C. Asplund, **M.R. Linford**,* Brigham Young University

We have recently developed a new and extemely rapid method for simultaneously functionalizing and patterning surfaces, which we term Laser Activation-Modification of Surfaces, or LAMS. This method consists of wetting a surface, e.g., Si or Ge, with a chemical and firing an intense, nanosecond pulse of laser light (355 or 532 nm) through the liquid onto the surface. The energy ablates a thin layer from the surface, exposing a highly reactive surface that appears to react instantaneously with the liquid it is in contact with. LAMS on silicon has been demonstrated with homologous series of 1-alkenes and 1-haloalkanes, and an epoxide and an alcohol. Unreactive compounds, such as octane and perfluorodecalin, also react in this manner; LAMS on Si with octane results in a functionalized surface. Surface modification is confirmed by X-ray photoelectron spectroscopy, time-of-flight secondary ion mass spectrometry, and chemical reactivity. Functionalized feature dimensions and morphology are shown by atomic force microscopy and imaging ToF-SIMS.

11:40am **SS+EM-WeM11 Temperature-Dependent Branching of Photochemical Reactions in Organic Layers and Biological Systems***, **M. Zharnikov**, A. Shaporenko,* Universität Heidelberg, Germany*; A. Baumer,* Walter Schottky Institut, Germany*; D. Menzel,* Technische Universität München, Germany*; P. Feulner,* TechnischeUniversität München, Germany

Radiation-induced damage represents a severe constraint for the characterization of organic materials, biological macromolecules, and cells by advanced electron or x-ray spectroscopy and microscopy. A possibility to reduce irradiation-induced degradation is cooling of the samples down to cryogenic temperatures. However, although the protecting effect of sample cooling against radiation damage is empirically well demonstrated, no detailed knowledge on its exact microscopic mechanism exists as yet. It is commonly assumed that the main effect is simply hindrance of mass transport in the object, whereas the basic irradiation-induced bond cleavage is believed to be unaffected. To prove this hypothesis we studied radiation damage of self-assembled monolayers, which are prototypes of thin organic layers and highly organized biological systems. We demonstrate that the effect of cooling is twofold. It freezes the structure, but by decreasing the mobility of fragments it also changes the branching of various photochemical reactions, thereby strongly modifying the cross sections as well as the products of irradiation induced processes. Two limiting cases could be identified. Reactions involving transport of single atoms and small fragments proceed nearly independent of temperature. Reactions requiring transport of heavy fragments are, however, efficiently quenched by cooling. We speculate that bonds can recombine if the fragments are forced to stay in place due to their reduced mobility at low temperatures. The results have direct implications for cryogenic approaches in advanced electron and x-ray microscopy and spectroscopy of biological macromolecules and cells.

Surface Science
Room 200 - Session SS1-WeM
Growth and Alloying of Surfaces

Moderator: K.F. McCarty, Sandia National Laboratories

8:20am **SS1-WeM1 Surface Alloy Compositions with Temporal and Spatial Resolution***, J.B. Hannon,* IBM Research Division*; **J. Sun**,* University of New Hampshire*; G.L. Kellogg,* Sandia National Laboratories*; K. Pohl,* University of New Hampshire

Controlling the composition of thin-film alloys is critical in a wide range of technologies. However, measuring alloy compositions at surfaces is difficult. Quantitative information on surface alloy compositions can be obtained from analysis of low-energy electron diffraction intensity versus energy spectra (LEED-IV). However, so far the structure and composition had to be assumed as spatially uniform. In this presentation we will describe low-electron energy microscopy (LEEM) studies on the formation of the well-known CuPd surface alloy phase grown on Cu(001). We will show how the presence of steps in the growth process makes the alloy layer inherently inhomogeneous. These variations in the CuPd alloy composition introduce strong measurable changes in the electron reflectivity in the regions around steps. By analyzing spatially resolved IV curves taken every 10 nm along a scan line normal to a step, we have determined the local surface alloy composition in the first 3 layers by using the average t-matrix approximation on a c(2x2) grid. In the process we are simultaneously optimizing both structural and non-structural parameters, while special emphasis is given to characterize the individual error bars of the method. We have investigated the composition on the terrace, far from steps, and the step-induced inhomogeneous structure caused by the step-flow growth. Depositing Pd at 500 K will cause an exponential increase of the Pd concentration with time and the formation of a c(2x2) Pd checkerboard structure in the 2nd Cu layer up to a 50% Pd concentration; far from the steps where the alloy is spatially uniform. However, during growth the steps flow over the 2nd layer Pd alloy, bury it and convert it to a 3rd layer alloy. This 3rd layer Pd is immobile and its concentration increases exponentially toward the step edge along the upper terrace, in agreement with the step-flow-growth model.

8:40am **SS1-WeM2 Formation and Vibrational Entropy-Driven Disordering of Mo(100) and W(100) Surface Alloys***, K.L. Man, Y.J. Feng, C.T. Chan,* Hong Kong University of Science and Technology*; **M.S. Altman**,* Hong Kong University of Science and Technology, Hong Kong

Atoms that are deposited on a surface of a dissimilar material may either remain on the surface or they may become incorporated in a surface or bulk alloy. Although the T = 0 energetic differences between alloy and overlayer structures can now be understood from first principles in many systems, entropy differences should also be revealed in the formation and stability of alloy versus overlayer structures. However, the entropic contribution to the system free energy is much less well understood than the energetic. The formation and stability of Cu, Ag and Au-induced c(2x2) alloys at the Mo(100) and W(100) surfaces have been investigated with low energy electron microscopy and diffraction. The dependence of the c(2x2) diffraction intensity upon metal deposition flux reveals that alloy formation is governed by atomistic processes that are analogous to those that dictate overlayer island nucleation. A second-order order-disorder transition is also observed that converts the surface from ordered alloy to disordered overlayer structure. Combined with knowledge of energetics obtained from first principles calculations, a comparison of disordering temperatures for alloys of the different metal species and substrates provides information on the vibrational entropic contribution to the system free energy. Effective Debye temperatures for metal adatoms are determined that are substantially lower than bulk values, but exhibit the expected mass dependence. Knowledge of the vibrational properties of metal adatoms should also be relevant to other common surface phenomena such as diffusion and desorption.

9:00am **SS1-WeM3 Bulk/Surface Mass Exchange and the Special Role of Bulk Dislocations in the Growth of NiAl Alloy***, **J.P. Pierce**, K.F. McCarty, N.C. Bartelt,* Sandia National Laboratories

When aluminum atoms are deposited on the surface of an Al-depleted NiAl crystal at high temperatures (> 900 K), new layers of NiAl alloy grow on the surface. We directly observe the appearance of new alloy by watching atomic steps advance across the surface using low-energy electron microscopy (LEEM). This behavior means that while Al atoms are delivered to the surface by our evaporator, Ni atoms are supplied to the surface by the bulk of the crystal. The competition in the arrival rates of these species determines how the surface evolves. At low temperatures (< 750 K), Ni atoms are unable to diffuse to the surface fast enough to accommodate the incoming Al atoms, so the Al atoms form a film on top of the alloy. At intermediate temperatures (750 to 900 K), we find that dislocations play a special role in transporting mass between the surface and the bulk. Al deposition causes the composition (i.e., the relative concentration of Al and Ni) at the surface to reach a critical level at which the points where bulk dislocations terminate on the (110) surface begin to move linearly. The dislocations provide a channel for mass exchange between the surface and the bulk; as the dislocations move, new crystal is left in their wake. As predicted by the one-dimensional diffusion equation, we find that the duration of Al exposure required bring the surface to the critical composition for dislocation motion grows as the inverse square of the Al flux. This confirms that the behavior on the surface is indeed limited by the diffusion of atoms through the bulk. We use our observations to identify the point defects that allow the Ni and Al atoms to diffuse and use the one-dimensional diffusion model to determine how the depth profile of the relative concentration of Ni and Al atoms evolves with time as the crystal tries to equilibrate. This work was supported by the Office of Basic Energy Sciences, Division of Materials Sciences of the U.S. DOE under Contract No. DE-AC04-94AL85000.

9:20am **SS1-WeM4 Real-Time Microscopy of Phase Transitions on Pb/Ge(111)***, **S. Chiang**, Y. Sato,* University of California, Davis

Using low energy electron microscopy (LEEM), we have elucidated the phase diagram for the growth of Pb on Ge(111). The Pb layer can form two stable @sr@3x@sr@)R30° phases on the surface, less dense @alpha@ and denser @beta@ phases. As Pb is deposited on Ge, the Pb atoms substitute into the top layer, causing released Ge atoms to form into c(2x8) adatom islands, with the size and density of these Ge islands controllable by the substrate temperature. With 11.6 eV electrons at 300C, we see the growth of the white (1x1) phase with respect to the darker @alpha@ phase in a coexistence region. During the reversible @beta@ to (1x1) phase transition, we discovered a novel phase separation mechanism. Above the 1.33ML @beta@ saturation coverage, a sharp first order phase transition is observed near 295C. For Pb coverage just <1.33ML, the @beta@ to (1x1) phase transition is no longer sharp, with the @beta@ and (1x1) phases coexisting and the transformation occurring from 232C to 181C. Reducing coverage by ~0.01ML causes a dramatic change. When the transition starts, small domains of the new phase appear and disappear, due to fluctuations between the two phases. As the initial domains stabilize in the new phase, additional domains appear and fluctuate until the whole surface is completely transformed. By using statistical mechanics analysis,@footnote 1@ we attribute the fluctuating domains to thermal fluctuations of the density of Pb atoms within a domain. By comparing LEEM images of the @beta@ and (1x1) phases during the phase transition between [@alpha@+(1x1)] and (@alpha@+@beta@), the Pb coverage of the (1x1) phase at the eutectic point was determined to be ~1.29 ML. @FootnoteText@ @footnote 1@ N. Bartelt, Sandia National Laboratories, Livermore, CA.

9:40am **SS1-WeM5 Self-Organized Growth and Magnetism of Nanostructures at Surfaces***, **H. Brune**,* École Polytechnique Fédérale de Lausanne - EPFL, Switzerland **INVITED**

We will discuss the state-of-the-art of self-organized atomic beam growth at single crystal surfaces enabling one to create well ordered superlattices of metal islands with sizes going all the way down to the single atom limit. We will focus on mutual interactions between adsorbed atoms mediated by Friedel oscillations in the 2D electron gas of a surface state, and on static templates with a periodic modulation of the binding energy for the adsorbed species. The templates to be discussed are strain relief patterns in thin films of metals, semiconductors, oxides, and nitrides. We then show model systems suited to explore the ultimate density limit of magnetic information storage. These are Co islands self-assembled on Au(788). The temperature dependence of the zero-field susceptibility @chi@ shows that the homogeneity in the anisotropy K and in the moment M would permit sin-gle particle bits, and that mutual interactions between the monodomain particles are absent up to densities of at least 26 Tera particles/in@super 2@. We further show results on the anisotropy of bimetallic islands as a function of their composition.

10:20am **SS1-WeM7 Steering Induced Nanopatterning: Super Poisson Growth at Grazing Incidence***, **H. Wormeester**, F.L.W. Rabbering, B. Poelsema,* University of Twente, The Netherlands

Analysis of high-resolution LEED data of 40 ML Cu on Cu(001) deposited at various polar angles led to the conclusion that attractive forces between the surface and the incoming particles have a dramatic steering effect on the trajectory of the particle. Incoming particles are attracted towards protruding structures leading to increased roughness and the formation of 1D nanopatterns at grazing incidence deposition. Already in the submonolayer coverage range consequences of the steering effect is observed for grazing incidence deposition. The steering induced heterogeneous distribution of the incoming flux has been modeled by a combination of long range Van der Waals forces and EAM calculations. The resulting trajectories have been combined with kMC simulations taking into account a large variety of intra and inter layer diffusion processes. The simulations are in good accordance with diffraction measurements up to 40 ML at both normal and grazing incidence. The evolution of the 1D nanopattern at glancing incidence deposition in terms of the distance between the ripples, the anisotropy and the roughness has been studied. The roughness evolves from a layer-by-layer fashion in the initial phase towards a strongly roughened interface above 10 ML. At 30 ML the roughness turns out to be even larger than for a Possion distribution, i.e. super Poisson growth is observed. The steering effect thus implies the necessity of a very different view for understanding the morphology development in growth at oblique incidence.

10:40am **SS1-WeM8 Ostwald Ripening of Manganese Silicide Islands on Si(001)***, **M.R. Krause**, A. Stollenwerk, J. Reed, V.P. LaBella,* University at Albany SUNY

Theoretical considerations suggest that epitaxial MnSi thin films should order ferromagnetically on Si(001)@footnote 1@ and it has been demonstrated that Si can be made ferromagnetic well above room temperature by Mn ion implantation.@footnote 2@ These recent discoveries indicate that the Mn-Si system may have potential to be utilized as a spin injector in future spintronics devices. Therefore the deposition of Mn onto Si(001) in the submonolayer regime has been studied with scanning tunneling microscopy (STM) to gain insight into the bonding and energetics of Mn with Si. The as deposited Mn films at room temperature are unstructured. Upon annealing to 300-500°C no smooth films but clusters of Mn or Mn@sub x@Si@sub y@ form while between the clusters the Si(001)-(2x1) reconstruction becomes visible. With increasing annealing time the density of clusters per surface area decreases while the average size of the remaining clusters increases. The time dependence of the coarsening shows the typical characteristics of Ostwald Ripening (OR). The cluster density and average cluster size will be presented as a function of annealing time for different initial Mn coverages. The results will be discussed within the framework of the OR theory. @FootnoteText@ @footnote 1@H. Wu, et al. Phys. Rev. Lett. 92 237202 (2004). @footnote 2@M. Bolduc et al. Phys. Rev. B 71 033302 (2005).

11:00am **SS1-WeM9 Self-assembly of Aperiodic Nanostructures using Quasicrystal Surfaces as Templates***, **R. McGrath**,* The University of Liverpool, UK **INVITED**

Quasicrystals are metallic alloys which posess long-range order but not periodicity; hence they may display structural symmetries not observed in periodic materials. The surfaces of these materials offer opportunities for the fabrication of nanostructures and thin films which themselves have unusual symmetries and structures. In turn, measurements of such nanostructured systems may offer insights into the larger question of the relationship between physical properties and aperiodicity. Several such systems, ranging from individual atoms to nanoclusters to thin films, have been fabricated and are under investigation in our laboratory. The growth of Si on quasicrystal surfaces is one recent example. On the AlPdMn quasicrystal, at submonolayer coverages, individual Si atoms occupy a unique adsorption site; thus the Si atoms can be considered to be arranged in a two-dimensional quasiperiodic array. On decagonal AlNiCo, the Si atoms form 5-fold nanoclusters, again indicative of a preferred adsorption site. Another spectacular example is that of an ultrathin film grown by the deposition of copper atoms on the five-fold surface of the icosahedral Al@sub 70@Pd@sub 21@Mn@sub 9@ quasicrystal.@footnote 1@ STM images show that the in-plane structure comprises rows having separations of S=4.5Â±0.2 Ã. and L=7.3Â±0.3 Ã., whose ratio is the golden mean @tau@=1.618... within experimental error. The sequences of such row separations form segments of terms of the Fibonacci sequence, indicative of the formation of a pseudomorphic Cu film. Finally, we have recently demonstrated that pseudomorphic films can also be grown using magnetic elements such as Co, Fe and Ni. Atoms in a quasiperiodic pattern are predicted to form new types of frustrated structures; such films therefore offer the possibility of observing these novel magnetic effects. @FootnoteText@@footnote 1@J. Ledieu, J.T. Hoeft, D.E. Reid, J.A. Smerdon, R.D. Diehl, T.A. Lograsso, A.R. Ross and R. McGrath, Phys. Rev. Lett. 92 (2004) 135507.

11:40am **SS1-WeM11 Coexistence of Periodic and Quasiperiodic Order in a Two-Fold Al-Ni-Co Decagonal Quasicrystal Surface***, J.Y. Park, D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory*; R.A. Ribeiro, P.C. Canfield, C.J. Jenks, **P.A. Thiel**,* Iowa State University

The atomic structure of the two-fold surface of a decagonal Al-Ni-Co quasicrystal has been investigated using scanning tunneling microscopy (STM). In the bulk the decagonal quasicrystal is composed of quasiperiodic planes that are periodically arranged. Atomically resolved scanning tunneling microscopy images of the 2-fold (10000) plane reveal the presence of atomic rows along the 10-fold direction with an internal periodicity of 0.4 nm. The spacing between the parallel rows is aperiodic, with distances following a Fibonacci sequence and exhibiting inflation symmetry. The bias polarity dependence of the STM images reveals three electronically-different types of atomic rows. A bulk model for Al-Ni-Co shows excellent agreement with these STM observations, and indicates that Al sites have a higher tunneling probability than transition meta sites. These data are compared with previous results for both the 10-fold and 2-fold surfaces.

Surface Science
Room 203 - Session SS2-WeM
Reactions on Metals & Oxides

Moderator: B.E. Koel, University of Southern California

8:20am **SS2-WeM1 Reactivity of Oxygen on Au(111) in CO Oxidation*, B.K. Min*,** *A.R. Alemozafar, D.S. Pinnaduwage, X. Deng, C.M. Friend,* Harvard University

Characteristics of oxygen on Au(111) related to reactivity in carbon monoxide oxidation were investigated by X-ray photoelectron spectroscopy (XPS), high resolution electron energy loss spectroscopy (HREELS) and scanning tunneling microscopy (STM). Oxygen was deposited on the Au(111) surface between 200 K - 400 K via exposure to ozone. Depending on the adsorption temperature, different characteristics of oxygen (chemisorbed and oxidic) and surface morphologies were observed. The reactivity of the oxygen-covered Au(111) surface is strongly dependent on reaction temperature; highest reactivity is observed at 200 K. Additionally, oxygen deposited at 200 K is more reactive than oxygen deposited at 300 K and 400 K. These results suggest that both reaction temperature and characteristics of oxygen are important for the reactivity of Au(111) in carbon monoxide oxidation.

8:40am **SS2-WeM2 Modeling of Nanoscale Spatiotemporal Behavior in CO-oxidation on Pd(100)*, D.-J. Liu,*** *J.W. Evans,* Iowa State University

For CO-oxidation on metal surfaces, a few STM studies have begun to explore nanoscale spatial organization in titration reactions, and FIM studies have revealed propagation of near-atomically sharp reaction fronts. However, there has been almost no realistic atomistic modeling of such processes. Thus, we have developed such a model for CO-oxidation on Pd(100) exploiting DFT calculations and experimental data, e.g., on adspecies ordering, to accurately determine the small but significant lateral interactions between adspecies. Efficient kinetic Monte Carlo algorithms are developed to study model behavior. Below 300 K, the system can be characterized by coadsorption of CO and oxygen with different ordering structures. Between 300 K and 350 K, reaction occurs involving sharp moving fronts between domains of CO and oxygen. In this regime, chemical diffusion of CO is greatly inhibited due to strong interactions between adsorbates. (At higher temperatures, the interface between CO- and oxygen-rich domains becomes an extended chemical wave, familiar from PEEM studies, the profile reflecting the coverage dependent CO diffusion.) Finally, for nanoscale systems (such as field emitter tips or supported metal clusters), fluctuation-induced transitions between reactive and near-poisoned steady states were also analyzed.

9:00am **SS2-WeM3 Surface Reactivity Tailored by Electron Confinement or Surface Modifiers Probed at Micro and Nano-Scales*, M. Kiskinova,*** Sincrotrone Trieste, Italy **INVITED**

Most of the attempts to tailor the surface reactivity have focused on the creation of specific surface structures, where electronic perturbations are induced, or by chemical modification of the surface properties by adding small amounts of substances. Recently it has been shown that the chemical specific imaging, combined with laterally resolved structural characterizations is of vital importance for understanding key factors controlling the processes at the surface of complex systems and the related to that local reactivity. In the talk selected results obtained using chemical specific imaging, photoelectron micro-spectroscopy, low energy electron microscopy and scanning tunnelling microscopy will be presented and discussed. The effect of electron confinement in ultrathin films will be illustrated for Mg films with varying thickness at micrometer scales; they show sensible difference in the local oxidation rate, correlated to the periodic changes in the density of electronic states induced by quantum-well states crossing the Fermi level of the Mg film.@footnote 1@ The complexity of the realistic systems, where a rich variety of self-organized micro and/or nano-structures may form and coexist under reaction reactions will be illustrated using the results obtained with Rh surfaces modified with potassium or other metals.@footnote 2,3@. In will be shown that stabilization of the substrate surface reconstructions and mass transport driven self-reorganization processes are common phenomena, which may affect the composition and reactive properties of the surface at local microscopic scales. @FootnoteText@@footnote 1@ L. Aballe et al, Phys. Rev. Lett. 93, 2004, 196103. @footnote 2@ S. G@um u@nther et al, J.Chem. Phys. 117, 2002, 2923119; ibid. 119, 2003, 12503; J. Phys. Chem. 2005, in press. @footnote 3@ A. Locatelli et al, J. Am. Chem. Soc. 127, 2005, 2351.

9:40am **SS2-WeM5 Rh-promoted Decomposition of Methanol Adsorbed on Cerium Oxide Thin Films*, J. Zhou,*** *D.R. Mullins,* Oak Ridge National Laboratory

Metal nanoparticles supported on single crystal oxides are important model systems for industrial catalysts. Research has found that the oxide substrates can greatly influence the catalytic activity of metal particles supported on them. In our study we have found that the reverse may also be true, i.e. that Rh nanoparticles may influence the thermal decomposition of methanol adsorbed on the oxide. All of the experiments were performed under UHV conditions by temperature programmed desorption (TPD) and synchrotron soft X-ray photoelectron spectroscopy (SXPS). Methanol decomposition was first carried out on the substrate ceria films to differentiate its chemistry from that when Rh is present. SXPS indicates that methanol deprotonates to form methoxy as the only intermediate on the ceria surface. On fully oxidized ceria, chemisorbed methoxy produced methanol and formaldehyde at about 560 K. However, on reduced ceria films methoxy decomposed further to produce primarily CO and H@sub 2@. When Rh nanoparticles were added to the ceria films, methoxy decomposed to CO and H@sub 2@ regardless of the ceria oxidation state and formaldehyde formation was suppressed. The desorption temperatures and intensities of CO and H@sub 2@ were found to be dependent on the reduction of the ceria films. These results indicate that the Rh promotes the decomposition of methanol adsorbed on the ceria and that decomposition may be influenced by the diffusion of methoxy intermediates across the oxide to the metal particles. Research sponsored by the U.S. Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

10:00am **SS2-WeM6 Adsorption of NO2 on Ultrathin @theta@-Al2O3/AlNi(100) Film: the Formation of Nitrite and Nitrate Species*, J. Szanyi*,** *E. Ozensoy, C.H.F. Peden,* Pacific Northwest National Laboratory

The interaction of NO2 with an ordered @theta@-Al2O3/NiAl(100) model catalyst surface was investigated using temperature programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS). The origin of the NOx uptake of the catalytic support (i.e. Al2O3) in a NOx storage catalyst is identified. Adsorbed NO2 is converted to strongly bound nitrites and nitrates that are stable on the model catalyst surface at temperatures as high as 300 and 650 K, respectively. The results show that alumina is not completely inert and may stabilize some form of NOx under certain catalytic conditions. The stability of the NOx formed by exposing the @theta@-Al2O3 model catalyst to NO2 adsorption increases in the order: NO2 (physisorbed or N2O4) < NO2 (chemisorbed) < NO2- < NO3-.

10:20am **SS2-WeM7 Correlation Between Electronic Structure and Chemical/Catalytic Reactivity of TiO@sub 2@(110) Supported Vanadia Catalysts*, S. Lee,*** Texas A&M University*; G.W. Zajac,* Innovene Corporation*; D.W. Goodman,* Texas A&M University

The adsorption and reaction of ethanol on model catalysts comprised of vanadium and vanadia deposited on rutile TiO@sub 2@(110) have been studied using temperature programmed desorption (TPD), X-ray and UV photoelectron spectroscopy (XPS and UPS), metastable impact electron spectroscopy (MIES), and low energy electron diffraction (LEED). Vanadium and vanadia films were prepared on TiO@sub 2@(110) under UHV conditions and the changes in their electronic properties were monitored following the adsorption and reaction of ethanol. Comparisons are made to Density of States generated from DFT calculations of small slabs of VO@sub x@/TiO@sub 2@ (Rutile) via the commercial codes of CASTEP and DMOL@super 3@ from Accelrys Inc. Dissociative adsorption of ethanol leads to the formation of ethylene at 650 K on TiO@sub 2@ supported vanadium. The activity for this reaction was found to depend markedly on the vanadium oxidation state.

10:40am **SS2-WeM8 Catalytic Activity of WO@sub 3@ Clusters on TiO@sub 2@(110): Trimerization of Formaldehyde*, J. Kim,*** Pacific Northwest National Laboratory*; O.A. Bondarchuk,* University of Texas, Austin*; Z. Dohnálek,* Pacific Northwest National Laboratory*; J.M. White,* University of Texas at Austin*; B.D. Kay,* Pacific Northwest National Laboratory

The catalytic activity of supported, high surface area transition metal oxides (TMO) catalysts have been extensively studied. In contrast, only a few studies have been conducted on transition metal oxide clusters supported on well-ordered, singe-crystalline oxide surfaces In this study, the catalytic activity of WO@sub 3@ clusters deposited on a well-characterized TiO@sub 2@(110) surface was examined. The clusters were deposited via direct, thermal evaporation of WO@sub 3@. This deposition technique provides a reliable, carbon free source of W in the (6+) oxidation state as shown by X-ray photoelectron spectroscopy (XPS). Related scanning tunneling microscopy (STM) studies reveal that 600 K-annealed WO@sub 3@ clusters are monodispersed and ~1 nm in diameter. Temperature programmed desorption (TPD) of N@sub 2@ reveals that the structure of WO@sub 3@ does not changed significantly between 400 - 600 K. We have examined the adsorption of formaldehyde (H@sub 2@CO) on TiO@sub 2@(110) and on WO@sub 3@ (< 4 x 10@super 14@ WO@sub 3@/cm@super -2@) on TiO@sub 2@(110). On TiO@sub 2@(110), H@sub 2@CO adsorbs and desorbs molecularly for all coverages. On WO@sub 3@/TiO@sub 2@(110), the adsorption of H@sub 2@CO multilayers results in the catalytic formation of trioxane. The trimerization yield increases with the amount of adsorbed H@sub 2@CO and saturates for coverages exceeding ~10 ML. Submonolayer coverage of H@sub 2@CO do not yield any trioxane product. The yield increases linearly with the amount of deposited WO@sub 3@ and the reaction can be run repeatedly. @FootnoteText@ *Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

11:00am **SS2-WeM9 Growth and Reactivity of Palladium Oxide Thin Films***, **J. Wang**, E.I. Altman,* Yale University

Palladium has become the catalyst of choice for the catalytic combustion of hydrocarbons in low NOx gas turbines. Recent studies suggest that oxidized Pd is a more active catalyst for the complete oxidation of hydrocarbons. Our prior work on the oxidation of CO and C3H6 on oxygen-covered Pd(100) showed that on the more oxygen rich surface there existed a direct oxidation route for C3H6 that proceeds with a lower activation energy than dissociation to C followed by oxidation to CO2. It was impossible to increase the oxygen coverage much beyond the oxide-like monolayer by dosing with O2 or NO2 in UHV. Two approaches are carried out to access the regime where bulk PdO forms: oxidizing the Pd(100) using an oxygen plasma in UHV; and direct growth of PdO thin films. In the first approach, XPS showed that exposure to the plasma at 575 K created bulk PdO, while temperature programmed desorption (TPD) showed an order of magnitude increase in the amount of oxygen compared to NO2 exposure. The reactivity of C3H6 on such surfaces is studied using TPD, isothermal kinetic measurements, and LEED. TPD is used to measure adsorption/reaction kinetics; mass spectroscopy to search for potential reaction products. Isothermal oxygen titration studies are performed by loading oxygen and then exposing to the reductant at fixed temperatures, which yields reaction rates versus oxygen coverage at constant temperatures, repeating the experiments at different temperatures yields activation energies. In the second approach, single crystal PdO(001) films are grown on MgO(100) substrate using oxygen plasma assisted molecular beam epitaxy (OPA-MBE). In situ reflection high energy electron diffraction (RHEED) is used to monitor the growth. Ex situ XRD, LEED, XPS and UPS are used to study the bulk and surface orientation, the surface composition and chemical states. The reactivity of the epitaxial films towards C3H6 will be compared with that of the poorly ordered PdO formed by oxidizing Pd(100).

11:20am **SS2-WeM10 Growth and Catalytic Activity of Epitaxial Palladium(111) Films***, **Z. Dohnalek**, J. Kim, B.D. Kay,* Pacific Northwest National Laboratory

Thin Pd films of various thickness were deposited on FeO(111) and Pt (111) substrates at 40 K. The morphology of the resulting films was characterized using low energy electron diffraction, Auger electron spectroscopy, and Kr and CO temperature programmed desorption as a function of annealing. The Pd layers deposited on Pt(111) are stable and develop into a well ordered Pd(111) films at annealing temperatures ranging from 500 to 1000 K. The Pd films deposited on FeO(111) can be ordered by annealing to 500 K but dewet upon heating to higher temperatures. The efficiency of ethylene hydrogenation was examined on these films as a function of their thickness and surface order. As the Pd(111) film thickness is decreased from 100 to 3 monolayers (ML), only a small increase (1 to 2%) in the hydrogenation efficiency is observed. This implies that H diffusion into the bulk does not play an important role for the films in this thickness range. A dramatic increase in the hydrogenation efficiency, resulting in yields up to 50%, occurs on the films covered with a disordered Pd layer (0-2ML) deposited at 40 K suggesting that the hydrogenation reaction is a structure dependent reaction. @FootnoteText@ Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

11:40am **SS2-WeM11 Structure-Activity Relationship: The Case of CO and CO@sub 2@ Adsorption on ZnO(0001), H/ZnO(0001), Cu/ZnO(0001)***, J. Wang, S. Funk, B. Hokkanen, E. Johnson,* North Dakota State University*; **U. Burghaus**,* North Dakota State University, Cass

Molecular beam scattering techniques were combined with thermal desorption spectroscopy (TDS) and applied to a number of different Zn-terminated ZnO systems; namely, clean ZnO(0001), defected ZnO(0001), H precovered ZnO(0001), and Cu precovered ZnO(0001). Furthermore, CO and CO@sub 2@ have been used as probe molecules with the goal to address the Structure-Activity Relationship (SAR). The CO@sub 2@-TDS curves consist of two distinct structures. By modifying the surface with Ar+ ion sputtering (more defects) and H-preadsorption (fewer defects), the two TDS structures could be assigned to adsorption of CO@sub 2@ on pristine and intrinsic defect sites with binding energies of 34.4 kJ/mol and 43.6 kJ/mol, respectively. Furthermore, He atom reflectivity curves indicated adsorption of CO@sub 2@ on defects. Thus, a kinetic SAR is evident. (See, Chemical Physics Letters 403 (2005) 42). Furthermore, a dynamic SAR was present in CO adsorption on the Cu/ZnO(0001) model catalyst. Whereas on small Cu sized-deposits, direct Langmuirian adsorption dynamics were observed; larger cluster sizes lead to the detection of precursor mediated adsorption dynamics of CO. Thus, the energy transfer processes governing the adsorption of a gas phase species on the surface depended distinctly on the morphology of the metal-on-metal oxide system. In the case of CO@sub 2@-Cu/ZnO(0001) a strong metal support interaction was observed; TDS and beam scattering data provide consistent hints that CO@sub 2@ populates predominantly along the rim of the Cu clusters. Monte Carlo Simulations have been applied for modeling of the molecular beam scattering data.

Thin Films

Room 310 - Session TF+EM-WeM

In-Situ/ Ex-Situ & Real- Time Monitoring

Moderator: V.M. Bermudez, Naval Research Laboratory

8:20am **TF+EM-WeM1 In-situ Infrared Absorption Spectroscopy of High-k Dielectrics Growth on Semiconductors***, **Y.J. Chabal**, S. Rivillon, Y. Wang, K. Bratland, M.-T. Ho,* Rutgers University **INVITED**

Atomic Layer Deposition (ALD) is a particularly attractive method to grow a variety of heterostructures on semiconductors. It makes it possible for instance to deposit ultra-thin and near stoichiometric high-k dielectric metal oxides films one layer at a time in a highly conformal manner. For microelectronics applications, controlling the nature of the semiconductor/oxide interface and the oxide film itself is critical. For instance, formation of an interfacial SiO2 layer during metal oxide growth or incorporation of excess oxygen in the oxide is a major detriment to the performance of future MOSFETs. This talk discusses the use of in-situ infrared (IR) absorption spectroscopy to optimize silicon and germanium wafer pretreatments, to monitor interface formation during growth and to control the nature of metal oxides. For this work, a simple ALD reactor has been designed to be compatible with efficient transmission IR spectroscopy. The effects of surface chemical functionalization of H-terminated Si and Ge surfaces with Cl, NH3 prior to and thermal annealing after Al2O3 and HfO2 deposition have been investigated with emphasis on identifying the presence and bonding of oxygen at the interface. The mechanism for oxygen incorporation have been identified resulting in a much better control of the interface.

9:00am **TF+EM-WeM3 Real-time Sensing for Process Dynamics and Metrology in Tungsten Atomic Layer Deposition***, **L. Henn-Lecordier**, W. Lei, G.W. Rubloff,* University of Maryland

Atomic layer deposition (ALD) has been investigated using a novel wafer-scale reactor which features an internal mini-reactor and in-situ mass spectrometry (MS) for chemical analysis during tungsten ALD using WF6 and SiH4. Downstream MS sampling system measures deposition kinetics directly and reaction product MS signal is used for real-time thickness metrology. MS signal reveals ALD reactant and product species in real time through ALD process cycle, with product generation and reactant depletion indicative of species consumption. Both the H2 product from SiH4 exposure and the SiF4 product from WF6 exposure show the kinetics of self-limiting adsorption/reaction on the surface, which enables process optimization to minimize cycle time. MS data also directly indicates the influence of process temperature and precursor dose on film growth, and can also been employed for process optimization. The integrated reaction product MS signal over each exposure, when plotted against ALD cycle number, reveals different stages of ALD film growth and provides a quantitative measure of film thickness. Our study demonstrated that integrated reaction product MS signal has a good linear relationship with ALD film thickness. This provides a promising approach to advanced process control in ALD manufacturing.

9:20am **TF+EM-WeM4 Twin Boundaries can be Moved by Step Edges during Film Growth*, N.C. Bartelt,*** *W.L. Ling, K.F. McCarty,* Sandia National Laboratories*; C.B. Carter,* University of Minnesota

Considerable effort has been devoted to minimizing twins in a film's microstructure because they typically degrade a film's performance. Twins are generally believed to originate from the nucleation stage of film growth. That is, when film islands nucleate, not all of them contain the same stacking sequence of film layers. Twin boundaries then occur where islands with different stacking sequence impinge. Attempts to reduce the density of twins are usually based on minimizing their nucleation or by removing them by annealing. We track individual twin boundaries in Ag films on Ru(0001) using low-energy electron microscopy (LEEM). We find that twin boundaries can move readily during film growth but relatively little during annealing. The growth-driven motion of twin boundaries occurs as film steps advance across the surface -- as a new atomic Ag layer approaches an fcc twin boundary, the advancing step edge carries along the boundary, which intersects the film thickness. This process can produce twin-free regions that are over 10 Âµm wide. These observations show that there can be a close connection between morphological evolution and microstructural evolution in thin films. This work was supported by the Office of Basic Energy Sciences, Division of Materials Sciences of the U.S. DOE under Contract No. DE-AC04-94AL85000.

9:40am **TF+EM-WeM5 In-Situ Real Time Spectroscopic Ellipsometry Studies of the Growth of Amorphous and Epitaxial Silicon for Photovoltaic Applications*, D.H. Levi,*** *C.W. Teplin, E. Iwaniczko, Y. Yan, T.H. Wang, H.M. Branz,* National Renewable Energy Laboratory **INVITED**

In-situ monitoring of material properties during thin film deposition provides researchers with a valuable tool for maximizing solar cell performance, while also enabling efficient exploration of deposition parameter space. In this presentation I will describe how our research team at NREL has utilized in-situ real time spectroscopic ellipsometry (RTSE) to maximize our productivity in two related projects. We are using hot wire chemical vapor deposition (HWCVD) for low-temperature (90 to 350@super o@C) deposition of very thin films of amorphous hydrogenated silicon (a-Si:H) for a-Si / crystal-Si (c-Si) heterojunction (SHJ) solar cells. We are also using HWCVD for low temperature (200 to 440@super o@C) deposition of epitaxial films of silicon (epi-Si) on c-Si substrates. We utilize RTSE as both an in-situ diagnostic and a post-growth analysis tool for SHJ solar cells and epi-Si films grown by HWCVD. RTSE enables precise thickness control of the 3 to 10 nm thick layers used in the SHJ devices, as well as monitoring crystallinity and surface roughness in real time. Post-growth analysis of the RTSE data has enabled us to determine the optical, electronic, and structural properties of the thin films used in the SHJ devices, as well as crystallinity vs. thickness in the epi-Si layers. This information has been used to fine-tune the deposition parameters to optimize device performance and epi-Si thickness. Using input from RTSE analysis we have achieved a photovoltaic energy conversion efficiency of 17% on an Al-backed p-type float-zone c-Si wafer. Epi-Si films have been grown as thick as 500 nm utilizing parameter optimization based on RTSE analysis.

10:20am **TF+EM-WeM7 Analytic First-Order Solution for the Simultaneous Determination of Complex Refractive Indices and Thicknesses of Thin Films Deposited on Substrates*, I.K. Kim,*** *D.E. Aspnes,* North Carolina State University

The problem of the simultaneous determination of the complex refractive index = n + i@kappa@ and thickness d of an isotropic thin film deposited on an isotropic substrate from polarimetric data (the so-called nkt problem) has never been solved analytically for a general , although solutions are available for the case of a transparent film (@kappa@ = 0). Here, we present an analytic solution for arbitrary n and @kappa@ that is valid to first order in d/@lambda@, where @lambda@ is the wavelength of light. The solution requires a knowledge of the change of pseudodielectric function <@epsilon@>, or alternatively the relative change @Delta@@rho@/@rho@ in the complex reflectance ratio @rho@, and either the relative change @Delta@Rp/Rp or @Delta@Rs/Rs, where Rp and Rs are the reflectances for p- or s-polarized light. Ranges of validity are obtained by comparing results to those obtained numerically using the exact three-phase-model expressions, and a procedure is presented for improving the accuracy. Numerical evaluation of the exact equations, which proceeds by least-squares analysis, is facilitated by using the first-order solution as a starting point. Depending on the sample the first-order solution is more effective at some energies than others, emphasizing the need for multiwavelength measurements over finite energy ranges. The most effective ranges can be determined from the correlation coefficients obtained in the least-squares analysis. As previously noted, the highest correlation generally occurs between n and d, although under some situations a high correlation can also occur between @kappa@ and d. The results should be particularly useful for systems involving reversible configurations, such as the cyclic adsorption and desorption of gases on clean surfaces, where accuracy can be improved by modulation techniques.

10:40am **TF+EM-WeM8 Linear Nanomechanical Measurements using a Novel AFM Technique*, P.M. Hoffmann,*** Wayne State University **INVITED**

Atomic Force Microscopy has been extensively used to study roughness, adhesion and mechanical properties of surfaces and thin films. However, commonly used AFM techniques suffer from a variety of problems inherent to the technique: Snap-in instabilities in static AFM and non-linearities in dynamic AFM measurements. Here we present a new AFM technique that avoids these problems and is capable of stable, linear measurements of many systems, including atomic scale contact mechanics and atomic friction on surfaces. I will introduce the technique and present recent results, especially the finding that continuum mechanics applies in atomic contacts even if the number of atoms in the contact becomes very low and the observation of friction due to a single atomic defect.

Thin Films

Room 306 - Session TF-WeM

Mechanical and Tribological Properties of Thin Films

Moderator: B.C. Holloway, College of William and Mary

8:20am **TF-WeM1 Mechanical Properties of Thin Films and Multilayers*, F. Spaepen,*** Harvard University **INVITED**

Thin films and multilayers are ideal systems to study the dependence of the mechanical properties on various length scales: grain size, film thickness, layer thickness, compositional modulation and dislocation cell size. Special techniques are required to perform tensile tests on thin films, which can be free-standing, or in the case of metallic films less than 1 mm thick, supported on thin, compliant polymeric substrates, such as Kapton. These techniqes allow determination of stiffness, anelastic behavior, yield stress, work hardening and fracture, all of which depend in characteristic ways on the various length scales. The development of stress in a thin film during deposition can be studied by measuring the curvature of the substrate (usually by laser reflection, often in situ) or the average lattice parameter (by X-ray diffraction). The development of the stress is strongly affected by the evolution of the microsctructure. Interfaces play a particularly important role. For example, the trade-off between surface and grain-boundary energies provides the (tensile) strain energy in island coalescence. Examples will be given from metallic (Cu, Ag,..) and ceramic (YSZ) films.

9:00am **TF-WeM3 Evaluation of Applied Substrate Bias on Yttria-Stabilized Zirconia Thin Films*, J.R. Piascik,*** University of North Carolina at Chapel Hill and RTI International*; J.Y. Thompson,* University of North Carolina at Chapel Hill*; C.A. Bower,* RTI International*; B.R. Stoner,* RTI International and University of North Carolina at Chapel Hill

Partially stabilized zirconia (PSZ), possesses a unique set of material properties. Due to its high toughness, excellent wear behavior, and thermal stability, PSZ, in the form of thin films, can be used for a variety of applications ranging from biomedical to thermal barriers. The objective of this research was to study environmental effects on film stress and model water absorption into the defect structure of films deposited with varying substrate bias. Yttria (3 mol%)-stabilized zirconia (YSZ) thin films were deposited using radio frequency (RF) magnetron sputtering. YSZ thin films were deposited at a working pressure of 15mT, temperature of 150°C, and Ar/O2 gas ratio of 30:1. An applied substrate bias was varied (0 to 50W) to alter film density and structure. X-ray diffraction (XRD) showed that films increased in monoclinic phase percentage as a function of increasing substrate bias power. Wafer bow measurements indicate that initial film stress increased in a compressive direction (70 to 302MPa) as substrate bias was increased. Aging in ambient environments (25°C, 75% relative humidity) led to a significant increase in compressive stress (80MPa) for films deposited without substrate bias. Thermal treatment, to remove absorbed water, caused films to return to near-initial stress states. Once exposed to ambient conditions, measured stress was found to increase at a rate of 0.20MPa/min for the first 2hr of exposure then by approximately 2MPa/day for a period of 30 days. Films deposited with applied substrate bias displayed a reduction in this time-dependent phenomenon. Cross-sectional TEM allowed for high-resolution images to analyze film structure and defect density. A subsequent model is proposed, describing the incorporation of water vapor into structural defects in the deposited films. This work is supported through NIH-NIDCR R01 DE013511.

9:20am **TF-WeM4 Ion Beam Assisted Deposition of Cubic Zirconia***, X. Wang,* University of Nebraska-Lincoln*; I. Amirani, S. Varma,* University of Nebraska Medical Center*; D.W. Thompson,* University of Nebraska-Lincoln*; F. Namavar,* Universoty of Nebraska Medical Center*;* ***N.J. Ianno,*** University of Nebraska-Lincoln

Cubic zirconia's excellent wear properties and inertness make it an excellent choice for a range of applications. In this work we will show that ion beam assisted deposition (IBAD) of thin film single phase cubic zirconium oxide has been accomplished. Deposition is accomplished by electron beam evaporation from a pure zirconium oxide source in a low pressure oxygen ambient coupled with simultaneous argon ion beam bombardment of the growing film. We will show that by proper control of the deposition parameters the grain size can be varied in a continuous manner from micron scale at the film-substrate interface to the nanometer scale at the film surface. This microstructure results in a film with an extremely high hardness. The deposited films will be characterized by x-ray diffractometry, atomic force microscopy, interferometry, transmission electron microscopy and spectroscopic ellipsometry.

9:40am **TF-WeM5 Effects of TiO@sub x@ PVD Deposition Parameters on the Preferred Orientation and Adhesion of Pt Films on @gamma@-Al@sub 2@O@sub 3@***,* ***E. Derniaux,*** ONERA France*; P. Kayser,* ONERA France, FRANCE*; C. Gageant, C. Sanchez, D. Boivin,* ONERA France

PVD TiO@sub x@ films are studied in order to improve the adhesion of Pt/AlN/Pt piezoelectric transducers on @gamma@-Al@sub 2@O@sub 3@/NiCoCrAlY/superalloy components. Thick (2 µm) TiO@sub x@ films deposited by RF reactive cathodic sputtering on @alpha@-Al@sub 2@O@sub 3@ substrates were analysed by X-ray diffraction (XRD) and scanning electron microscopy equipped with X-ray spectroscopy (SEM/EDX). The influence of substrate temperature, O@sub 2@/(Ar+O@sub 2@) ratio in the plasma gas and annealing (1050°C, 1h, in air) on structural properties, morphology and chemical composition was observed. Thin (@<=@100 Å) TiO@sub x@ adhesion layers and Pt films were sputtered on @alpha@-Al@sub 2@O@sub 3@. The effects of TiO@sub x@ deposition parameters on the adhesion and the orientation of as-deposited and annealed Pt films were examined respectively by pull off test and XRD. Results showed the (111) preferred orientation and the good adhesion of Pt films. Finally, the selected TiO@sub x@ deposition parameters were applied on @gamma@-Al@sub 2@O@sub 3@/NiCoCrAlY/superalloy substrates. Adhesion properties of annealed Pt films on @gamma@-Al@sub 2@O@sub 3@ and TiO@sub x@/@gamma@-Al@sub 2@O@sub 3@ were evaluated, the results showed a drastic improvement of the pull off force (0 to 1000 kg.cm@super -2@) by using the TiO@sub x@ 'glue layer'. The adhesion layer led also to a higher (111) preferential orientation of the Pt films.

10:00am **TF-WeM6 Microstructure and Stress of Room Temperature Reactively Sputtered RuOx Thin Films***, J. Shi,* ***T.M. Klein,*** The University of Alabama

RuOx thin films were deposited at room temperature by reactive RF magnetron-sputtering using Ar/O2 discharges of varying O2 flow ratio (O2/Ar+O2) over the range 10% to 50%. With an increase of O2, the film texture changed from (110) to (101). Films deposited with a flow ratio >25% were determined stoichiometric. Apparent grain sizes, densities and hardnesses by nanoindentation were measured as a function of flow ratio. Deposition rate, resistivity and intrinsic stress trends with O2 flow ratio were similar. The intrinsic stresses in as-deposited films were all compressive and increased with addition of O2, except for the film sputtered at a flow ratio of 20% which was in biaxial tension. Stress-temperature behavior during a thermal cycle in air up to 500ÂºC changed for films deposited at different flow ratios due to varying microstructure evolution. The film deposited at a flow ratio of 30% became nearly stress-free with a low resistivity value of 68 micro Ohm-cm after anneal which is promising for use in micro-devices.

10:20am **TF-WeM7 Synthesis of Carbon Films with Ultralow Friction in Dry and Humid Air***,* ***C.A. Freyman,*** *Y.F. Chen, B. Zhao, Y.W. Chung,* Northwestern University

In this paper, we present experimental strategies of how one can synthesize smooth carbon films using sulfur doping with ultralow friction coefficients (µ< 0.01) in dry and humid air, with relative humidity up to 50%. Auger studies show the absence of water adsorption after room temperature water exposure of 100,000 Langmuirs. Thermal desorption studies suggest the formation of water multilayers even at very low exposures, indicating that the surface is hydrophobic, consisting with water contact angle measurements. Results from quartz crystal microbalance studies at ambient pressures will also be discussed.

10:40am **TF-WeM8 Surface Modification of Si@sub 3@N@sub 4@ Probes for Adhesion and Wear Reduction***,* ***Z. Tao****, B. Bhushan,* The Ohio State University

Tip wear of Si@sub 3@N@sub 4@ probes used for atomic force microscope (AFM) can result in increase of tip radius, thus reducing the image resolution and introducing artifacts. Adhesion between the tip surface and sample is another source of image artifacts. In order to reduce adhesion and wear, perfluoropolyether (Z-TETRAOL) and Fluorinert@super TM@ will be deposited on the Si@sub 3@N@sub 4@ probe. The adhesion, friction, and wear of the uncoated/coated tips will be investigated. The humidity effects on the adhesion, friction, and wear of the uncoated/coated tips will be investigated as well. The influence of the coating on the image resolution will be discussed.

11:00am **TF-WeM9 Ultra-Hard Al-Si Nanocomposites Synthesized by High-rate Co-evaporation***,* ***D. Mitlin****, C. Ophus,* University of Alberta, Canada*; V. Radmilovic, T.J. Richardson, U. Dahmen,* Lawrence Berkeley National Laboratory

We used high rate co-evaporation to synthesize Al-Si nanocomposite films in the composition range of Al-1at%Si to Al-23at.%Si. Pure Al films were also synthesized using identical deposition conditions, and were used as a baseline. The Al-Si structures have a hardness as high as 4GPa (Al-23at.%Si), and display noticeable plasticity under nanoindentation (Al-12at.%Si). We used transmission electron microscopy (TEM) to analyze Al-12at.%Si and pure Al samples. The pure Al film had the expected grain size of upwards of one micrometer. The Al-Si film consists of a dense distribution of spherical nanoscale (10-30 nm) Si particles separating irregularly-shaped Al grains, many of which are also nanoscale (50-200 nm). This microstructural refinement is due to the Si particles disrupting the columnar growth of the Al grains by promoting re-nucleation. Additionally the particles also pin the Al grains which coarsen during deposition. X-ray diffraction results indicate that there is a marked decrease in the Al lattice parameter with increasing Si content. This effect is weaker after the samples have been stored at room temperature for six months. The structures' electrical resistivity remains near the level of pure Al for compositions up to 6.5at.%Si, but significantly increases at higher Si compositions. This work is the first step towards yielding Al-Si nanomaterials specifically optimized for integration into structural components of MEMS.

11:20am **TF-WeM10 Hard Coatings of Tungsten Nitride Grown by Reactive Sputtering and Laser Ablation***,* ***E.C. Samano****, A. Clemente, M.J. Oviedo, G. Soto,* CCMC-UNAM, Mexico

The search for materials showing chemical inertness and high hardness, elastic modulus and melting point is still intense. Transition metal nitride coatings are an alternative because they have been traditionally used as protective coatings against wear and corrosion. Due to the fact that refractory metals are hard materials with a high melting point, tungsten nitride coatings are an excellent choice. Their properties can be tailored by tuning the nitrogen content during film synthesis. The investigation on the relationship between thin film preparation conditions and mechanical properties for tungsten nitride films is not as well understood as other transition metal nitrides, like titanium nitride. We report the growth of tungsten nitride films grown by two different deposition methods, reactive sputtering and laser ablation, in the ambient of N@sub 2@ at various pressures on stainless steel substrates. The composition of the films is determined by AES and XPS. The stoichiometry of the coatings grown by reactive sputtering are found to be W@sub2-x@N, 0@<=@x@<=@0.5, while those grown by laser ablation are W@sub2@N, WN and WN@sub2@. The mechanical properties of the films grown by both deposition methods are studied as a function of N@sub2@ pressure. The hardness of the deposited films resulted to be in the 25 to 35 GPa range.

11:40am **TF-WeM11 Electron Spectroscopic Studies of Friction Modifier Thin Films*, K.C. Wong,*** University of British Columbia, Canada*; X. Lu,* Kelsan Technologies Corp.*; P.C. Wong,* University of British Columbia, Canada*; J. Cotter, D. Eadie,* Kelsan Technologies Corp.*; K.A.R. Mitchell,* University of British Columbia, Canada

Friction modifier (FM) thin films are important for controlling friction at the wheel-rail interface of trains. Products on the market have progressed to date largely by empirical development. Accordingly we have initiated a program to investigate how FM model systems are affected by tribological experiments that simulate wheel-rail contact using a rolling disk-on-disk setup adjusted for designated pressure and creepage. This paper will report spectroscopic characterizations (with XPS, Raman and SAM) and thermogravimetric analyses for FM materials (e.g. MoS2, graphite, BN, WS2, ZnO, MoO3, talc, SnO2, polytetrafluoroethylene, polyimide and polyamide) and water-based emulsion polymers as binders, where the studies are made as a function of coefficient-of-friction, number of rolling cycles and temperature.

Vacuum Technology
Room 201 - Session VT-WeM
Gas Flow and Pump Technology

Moderator: R. Langley, Oak Ridge Science Consultant

8:20am **VT-WeM1 Pressure Dependence of Laminar-Turbulent Transition in Gases*, L.D. Hinkle,*** Falmouth Public Schools*; A. Muriel,* World Laboratory, CERN*; S.A. Novopashin,* Institute of Thermophysics, Russia **INVITED**

The transition between the laminar and turbulent flow regimes is traditionally addressed using the continuum formulation of the Navier-Stokes equation and dimensionless parameters such as the Reynolds number. However, a detailed understanding of the transition mechanisms has remained elusive. Theoretical approaches based on molecular and quantum mechanical models have been proposed but have yet to be thoroughly tested experimentally. In an effort to test a quantum-based model, specific apparatus and experiments have been designed to evaluate particular features of the laminar-turbulent transition. The experiments and analysis examine the transitions by producing a hysteresis plot as displayed on a flow versus differential pressure graph. This has been done for the transitions occurring in a tube with a divergent entrance. The hysteresis plots generated in these tests show several notable features and quantitative trends. The primary focus of this paper is on the observed absolute pressure dependence of the transition behavior. Whereas the continuum-based model does not predict a pressure dependence of the laminar-turbulent transition, a relatively simple quantum-based model indicates a particular pressure effect on the transition to turbulent flow.

9:00am **VT-WeM3 The Nanogate as a Nanoscale Variable Flow Leak Element***, J.R. White, **P.J. Abbott**, M.J. Tarlov,* NIST*; A.H. Slocum,* Massachusetts Institute of Technology

We present a variable flow leak artifact based on an ultra-high precision MEMS-based valve called a "Nanogate." Many critical industrial processes rely on generating and delivering accurate and precise flows of gas. Examples include leak testing of nuclear containment vessels, gas delivery in semiconductor processing, quantifying the emission of ozone-depleting chlorofluorocarbons, food processing and packaging, and testing of medical implants such as pacemakers. The flows of gas required for these applications span a very broad range, from as low as 10@super-14@ moles per second to higher than 10@super-6@ moles per second, and generally require several instruments to cover it; among these are mass flow controllers, metal capillary leak elements, and permeation leak elements. In contrast, the Nanogate can generate extremely low gas flows over several orders of magnitude, for any gas of interest, and offers the advantage of precise control of the flow rate due to the Nanogate's ability to change its opening in controlled two angstrom steps. Testing of the device with helium, carbon dioxide, and methane has shown good agreement with theory. Calibration results with several gases using the NIST low gas flow standard will be discussed.

9:20am **VT-WeM4 Thermal Fluid Dynamic Model of a Holweck Vacuum Pump Operating in the Viscous and Transition Regimes*, S. Giors,*** Varian Vacuum Technologies, Italy*; E. Colombo, F. Inzoli,* Politecnico di Milano, Italy*; F. Subba, R. Zanino,* Politecnico di Torino, Italy

Holweck drag pumps are used as high-pressure stages in hybrid turbomolecular pumps, where they operate in the transition and the viscous regime. In these regimes, thermal problems related to the viscous heating of the rotor become a major issue in the design of the pump. The fluid dynamic study of the Holweck pump was carried out by Boulon et. al.,@footnote 1@ using a three-dimensional no-slip Navier-Stokes model. They show a good agreement with the experimental data in the viscous regime, and they suggest the need of slip-flow boundary conditions to improve the accuracy for Kn > 0.01. The benefits of slip-flow boundary conditions for Kn > 0.01 are also confirmed by Giors et. al.,@footnote 2@ for a Gaede drag pump. In this work the emphasis is on the application of slip-flow boundary conditions to a single-stage Holweck pump model, and on the heat exchange phenomena occurring between rotor and stator. A three-dimensional thermal fluid dynamic model of the pumping grooves is developed, based on the Navier-Stokes equations, with viscous slip and thermal jump boundary conditions. Taking advantage of the high Biot number, a lumped-parameter heat conduction model of the solid parts of the pump is justified and coupled to the three-dimensional fluid dynamic model. A commercial CFD code is used to solve the conjugate heat transfer problem in the viscous and transition regimes and to predict the pressure profile along the grooves, together with the friction power and the rotor temperature. The numerical results are compared with the available experimental data and critically analysed. @FootnoteText@ @footnote 1@ O. Boulon, R. Mathes, Flow modeling of a Holweck pump stage in the viscous regime, Vacuum 60, 73-83 (2001).@footnote 2@ S. Giors, F. Subba, R. Zanino, Navier-Stokes modelling of a Gaede pump stage in the viscous and transitional flow regimes using slip-flow boundary conditions, J. Vac. Sci. Technol. A, 23(2), 336-346 (2005).

9:40am **VT-WeM5 Selective Water Vapor Cryopumping Through Argon***, A.P. Kryukov,* Moscow Power Engineering Institute, Russia*; **O. Podcherniaev**,* Helix Polycold Systems, Russia*; P.H. Hall,* Polycold Systems*; D.J. Plumley ,* Helix Polycold Systems, Russia, USA*; V.Yu. Levashov, I.N. Shishkova,* Moscow Power Engineering Institute, Russia

A selective cryopumping process for water vapor control takes place in vacuum systems for web coating or plasma operations; such as sputter deposition, etching, etc. Excessive water vapor content will affect quality of the processes and final products. These vacuum systems typically operate at pressures corresponding to transitional or viscous flow regimes, and water vapor cryopumping is highly limited by diffusion of water vapor molecules through a non-condensable process gas (argon, air). An analytical model was created to describe water vapor condensing process through a non-condensable gas diffusion barrier. The model accounts for the collisions of different molecules by means of Boltzmann kinetic equations for two-component rarefied gas. It was assumed that water vapor content is about three orders of magnitude lower than that of the non-condensable gas (argon). Cryopumping process was analyzed for two simplified cases when water vapor source and cryosurface are: parallel plates and coaxial cylinders. The calculations were conducted for different water vapor outgassing rates and argon pressures ranging from 0.5*10@super -3@to 20.0*10@super -3@ torr. At certain parameters a strongly non-linear distribution of water vapor pressure and density vs. distance between source and cryosurface was obtained. At high argon pressures an increase of water vapor pressure was observed nearby an outgassing surface. The results were used for calculation of water vapor cryopumping rates.

10:00am **VT-WeM6 The Effect of Heat Radiation on the Pumping Performance of Cryopump*, H.-P. Cheng*,** *Y.-H. Shen, C.-W. Sun,* National Taipei University of Technology, R.O.C.

In this study, the quartz lamp was placed at the center top of the vacuum chamber of the G-M Cryopump. Measurements of the throughput, pumping speed, and the temperature of the cryopanel surface inside the Cryopump based on different energy levels of the quartz lamp were taken, in order to discuss the effect of quartz lamp energy on the pumping performance after transmitted to the inside of the Cryopump by means of heat radiation. The test system was built based on the standard suggested by Welch, the tested Cryopump was ULVAC-10PU. Before the transmission of heat by the quartz lamp, the measured pumping speed for nitrogen was 1,573~2,423 Liter/sec when the chamber pressure was controlled at 2.0E-03~1.3E-01Pa, and the throughput were 1.71~171.52 SCCM. The first-stage cryopanel surface temperatures were 66.52~85.27K, second-stage cryopanel surface temperatures were 9.93~12.73K. After transmitting heat energy of 5, 10, 15, 20W by the quartz lamp, the pumping performance of the Cryopump deteriorated, the temperatures of first- and second- stage cryopanel surfaces increased, while the increase of first-stage cryopanel surface temperature was more significant. When nitrogen was used as the testing gas, the increase of temperature inside the Cryopump was most significant when the energy of the quartz lamp was 20W. When the chamber pressure was 2.0E-03~1.3E-01 Pa, the throughput in the chamber was 1.61~145.65 SCCM, the pumping speed dropped to 1,476~2,058 Liter/sec, the temperatures of first- and second- stage cryopanel surfaces increased from 103.03K and 12.03K to 126.03K and 14.9K, respectively. Based on the above data, when the heat radiation of quartz lamp was 20W, the temperatures of first- and second- stage cryopanel surfaces were reaching the upper limit of the standard suggested by Welch, thus, it is not recommended to increase the quartz lamp energy.

10:20am **VT-WeM7 A Comparison of Various Standards Proposed for the Measurement of the Speed of Sputter-ion Pumps*, S.P. Clough,*** Gamma Vacuum, LLC

A detailed comparison is made of the recommended procedures and equipment for measuring the speeds of sputter-ion pumps as proffered by: i) the ISO in DRAFT INTERNATIONAL STANDARD ISO/DIS 3556-1,2 (1992); ii) the DEUTSCHE NORM Acceptance specification for sputter-ion pumps DIN 28 429 (1985); and, iii) the AVS Recommended procedure for measuring pumping speed, no number (1987). The purpose of this work is to: highlight the concurrences and disparities between the "standards", ii) suggest reasonable criterion relating to procedures and equipment; and, iii) propose a more global template for such measurements.

10:40am **VT-WeM8 The Hydrogen Pumping Speed of Sputter-Ion Pumps*, K.M. Welch,*** Kimo M. Welch, Consultants*; S.P. Clough,* Gamma Vacuum

It is difficult to find consistent quantitative data for the hydrogen speed of a conventional diode sputter-ion pump. The reported numbers range from 80% to greater than 200% of the speed of the sputter-ion pump for nitrogen. Reported numbers are in part obscured by conductance considerations when comparing speeds for the two gases. For example, results of speed measurements on smaller pumps, with restricted input conductances, might yield higher relative hydrogen speeds than that observed with larger pumps. Also, relative speed measurements are further obscured by pump conditioning prior to the measurements. This paper first reviews the existing literature on reported hydrogen speeds of sputter-ion pumps for a variety of cathode materials. Thereafter, results are reported on comparative speed measurements for the two gases in tests on a larger pump. These data permit calculations of the actual intrinsic speeds of a unit-cell sputter-ion pump for the two gases., and therefore more reasonably predict expected speeds of multi-celled sputter-ion pumps.

11:00am **VT-WeM9 New High Capacity Getter for Large Vacuum Devices*, H. Londer,*** Alvatec Alkali Vacuum Technologies GmbH, Austria*; P. Adderley,* Jefferson Lab*; G. Bartlok,* MAGNA STEYR Fahrzeugtechnik AG & Co KG, Austria*; W. Knapp, D. Schleussner,* Otto-von-Guericke-Universitaet Magdeburg, Germany

Current Non evaporable getters (NEGs) are important for the improvement of vacuum by the help of metallic surface sorption of residual gas molecules. High porosity alloys or powder mixtures of Zr, Ti, Al, V, Fe and other metals are the base material for this kind of gas sorbents. The development of vacuum technologies creates new challenges for the field of getter materials. The main sorption parameters of the current NEGs, namely, pumping speed and sorption capacity, have reached certain level limits. Chemically active metals are the basis of NEGs of a new generation. The appearance of new materials with high sorption capacity at room temperature is a long-felt need. It is obvious, that chemically active metals and alloys with reactivity higher, than that of transition metals, can become this kind of materials. The potential of active metals as the strongest gas sorbents is very high. The improved getter materials allow a faster pumping speed and a significant higher sticking rate on the chemically active surface. The sorption capacity can be increased by up to 10@super 4@ times due to the active surface (during the life-time of a device the whole volume of the getter material reacts). Our directions are active metals with controlled insulation or protection. The main structural forms of the new getter concepts are spherical powders, granules and porous multi layers. The full sorption performance takes already place at room temperature, the activation temperature can be adjusted between room temperature and 650 degree C. The paper presents measurement- and analytical data of the sorption behaviour, like pumping speed, sorption capacity etc., of different residual gases, like H2, N2, O2, CO2, etc.. The comparison of the data with the existing getter technology shows several advantages and new fields of possible applications.

11:20am **VT-WeM10 Achieving Ultra High Vacuum By Backing Cascaded Turbo Pumps with NEG or Ion Pumps*, *P. Adderley,*** Jefferson Lab*; C. Day,* Forschungszentrum, Karlsruhe*; G.R. Myneni,* Jefferson Lab

The scientific community requires contamination free pumping systems to achieve low ultimate pressures in order to maintain low working pressures in a process or given application. Even though the turbo molecular pumps are able to achieve pressures in the ~5.e-11 Torr range, there are several disadvantages including back streaming, vibrations, oil-laden bearings of the traditional backing pumps. In this paper we present alternative backing methods, which will eliminate the above problems. In addition we will report the achievement of UHV pressures with cascaded conventional turbo pumps backed by ion, traditional NEG or the new active NEG pumps. *This work was supported by U.S. Department of Energy Contract No. DE-AC05-84ER40150 and KATRIN International Collaboration at FZK in Germany.

11:40am **VT-WeM11 A Micromachined Vapor-Jet Vacuum Pump with an Integrated Pirani Pressure Sensor*, M. Doms,*** *J. Müller,* Hamburg University of Technology, Germany

A MEMS vapor-jet pump is presented which is based on the well-known principle of vapor-jet and diffusion pumps. A high velocity gas- or vapor-jet is used for vacuum generation. The microfabricated pump consists of two planar Laval nozzles (20-40 µm nozzle width) and water cooled sidewalls. Presently an external supply of the working fluid is used (nitrogen gas, water vapor). As no mechanically moving parts are required, the pump system offers an advanced long-term stability. A detailed mathematical and physical description of the micro vapor-jet pump has been described elsewhere.@footnote 1@ Based on simulation results, various systems with different geometries have been designed, fabricated and characterized. Starting from atmospheric pressure, a high pumping speed of more than 2.8 ml/min and an absolute pressure of 495 mbar were generated with this new type of micropump. Lower pressure regimes will be accessible with a full integration of all components (internal working fluid evaporation, condensation and recirculation) and by the use of more appropriate working fluids and multiple nozzle stages. Different concepts for the working fluid recirculation based on porous silicon and active or passive pump mechanisms which are currently investigated will be presented. The size of the complete pump system will not exceed 15 x 15 x 2 mm. Microfabricated pressure sensors based on the Pirani principle have been integrated into the micropump to monitor and control its function. Due to its novel geometry and fabrication process the operating range of the sensors can easily be adapted to different pressure ranges without any change of the layout. An integrated full bride layout is used for temperature compensation. The characteristics of the sensors correspond well with theory and fully satisfy the specifications. @FootnoteText@ @footnote 1@M. Doms, J. Müller, A Micromachined Vapor-Jet Pump, Sens. Act. A, Vol. 119 No 2, Mai 2005, p. 462-467.

Exhibitor Workshop
Room Exhibit Hall C&D - Session EW-WeL

XPS and SPM New Developments and Applications

Moderator: C. Bryson, Apparati, Inc.

12:00pm **EW-WeL1 Improvement of the Quantification from XPS Data Using Predetermined Spectrometer-Transmission Functions with UNIFIT 2004***, **R. Hesse**, P. Streubel, R. Szargan,* University of Leipzig, Germany

The reliability of the quantification from XPS data was improved using calibrated intensity scales of the photoelectron spectrometer ESCALAB 220 iXL. Two different sub-routines, survey-spectra approach (SSA) and minimizing the error of the quantified peak-area approach of standard peaks (QPA), for estimating the transmission functions T(E) of different acquisition modes of any photoelectron spectrometers are integrated in the software UNIFIT 2004. For the method SSA the spectra from Au, Ag and Cu measured on the Metrology Spectrometer II of NPL have been used. The estimation of T(E) using the method QPA was carried out by means of the peak areas from Au 4f, Au 4d, Au 4p@sub 3/2@, Ag 3d, Ag 3p@sub 3/2@, Cu 3p, Cu 2p@sub 3/2@, Ge 3d and Ge 2p@sub 3/2@ lines measured for Mg K@alpha@ and Al K@alpha@ X-rays. The theoretical basis of quantification as well as the results of the transmission functions T(E) (E - kinetic energy) of the spectrometer have been considered for both approaches SSA and QPA.. In the presented paper the influence of pass energies (10 eV and 50 eV), lens modes (Large Area, Large Area XL, Small Area 150) and X-ray sources (Al/Mg-twin and Al-mono) on T(E) is discussed. It was found that the form T(E) = a+bE@super c@ (a, b, c - parameters) gives an appropriate approach to describe T(E) of the studied spectrometer modes in many cases. In order to demonstrate the applicability of the calculated functions T(E), a quantitative analysis of the sample Ni90Cr10 was performed. Keyword: UNIFIT, Spectrum analysis software, Photoelectron spectroscopy, Quantification, Transmission function, Intensity/energy response function.

12:40pm **EW-WeL3 Latest Development in Environmental Scanning Probe Microscope - Membrane of a HELA Cancer Cell***, S. Xu, **C. Wall**,* Molecular Imaging Corp.

The presentation will focus on the following topics: a) the environmental AFM application in chemistry, material science and biomaterial research; b) Nanografting: fabrication of nanometer size patterns using AFM and the potential application in development of biosensors; c) Post-imaging data processing, data rendering and analytical techniques; d)nanometer level mechanical testing application in biological materials. Many experiments benefit from imaging under controlled conditions: for biological applications imaging at 37 C is often crucial and controlled gas environments (oxygen, carbon dioxide etc) is frequently required. Electrochemical measurements are carried out in solution, mostly at the absence of dissolved oxygen, polymer studies are affected by humidity and temperature. In-situ real time "nano-movies" can be taken at programmed changing temperature between -40 C to +250 C. Various experimental results will be discussed using versatile imaging modes and under wide range of environmental controlling techniques. The concept of AFM nanolithography includes a list of surface chemistry reactions that could be used to create nanometer level patterns using atomic force microscope. Fabrication of nanometer size patterns attracted tremendous attention because patterned surfaces can be used as the building block for a wide range of research in developing biological sensors, nanodevices and masks for fabrication of nanoelectronics. Through chemically active nanopatterning, surfaces can be engineered with nanoscale spatial resolution. The concept of NanoGrafting includes a wide range of SPM assisted nanolithography techniques which could yield nanometer size patterns with desired chemical functionality on a variety of substrates. AFM images not only give a topographic view of the sample surface with high resolution, post-imaging processing can also allow researchers to extract more quantitative information of the experiments. Skillful data rendering not only can help the enhancement of spatial resolution, using Texture Mapping, advanced imaging mode data can be displayed with much more informative format and striking clarity.

1:00pm **EW-WeL4 Dynamic Scaling during Shadowing Growth of Ru Nanorods***, **L. Li**, F. Tang, T. Karabacak, G.-C. Wang, T.-M. Lu,* Rensselaer Polytechnic Institute

We present a comprehensive study of dynamic scaling behavior of ruthenium nanorods grown by oblique angle sputter deposition with substrate rotation. The vertical nanorod arrays with various lengths (~ 40 to ~ 480 nm) were grown on silicon substrates tilted with an angle ~85° from the surface normal of the sputtering target. The images of the nanorods were obtained by atomic force microscopy (AFM) and scanning electron microscopy (SEM). The images were analyzed using morphological analysis methods including power spectral density and autocorrelation functions. We observed that the Ru nanorods generated a quasi-periodic structure defined by a wavelength (@lambda@) as a result of shadowing effect. Moreover, the wavelength @lambda@, rod number-density N, rod diameter W, root-mean-square roughness @omega@, and lateral correlation length @xi@ (which measures an average distance within which the surface heights are correlated and is different from the wavelength) all change with rod height h according to a power law relationship, ~h@super p@, with exponents p@sub &lambda@ = 0.43 ± 0.02, p@sub N@ = -1.01 ± 0.02, p@sub W@ = 0.47 ± 0.09, p@sub &omega@ = 1.11 ± 0.01, and p@sub &xi@ = 0.55 ± 0.02, respectively. The measured values of the exponents p@sub W@, p@sub &omega@, and p@sub &xi@ are consistent with the results of theoretical models on oblique angle growth that include the effects of shadowing effect and isotropic surface diffusion. However, the exponents p@sub &lambda@ and p@sub N@ are not predicted by any previously known growth models. @FootnoteText@ F.T. is the recipient of the Harry Meiners Fellowship.

1:20pm **EW-WeL5 A New Approach to SPM Control Electronics***, **M. Maier**, B. Uder,* Omicron NanoTechnology, Germany

We developed a control system that couples advances in digital electronics with the requirements of the latest SPM applications to offer an extremely high level of experimental flexibility and data processing control. Fundamental to its modular philosophy are a series of advanced digital boards each equipped with CPU, DSP and logic elements. Programmable elements are "soft-wired" opening up to new functionality such as multi-channel feedback, input/output trigger control, pre-emptive feedback, and non-orthogonal and non-linear scan generation.

Applied Surface Science
Room 206 - Session AS-WeA

SIMS Cluster Probe Beams and General Topics

Moderator: I.S. Gilmore, National Physical Laboratory, Australia

2:00pm **AS-WeA1 Analysis of a Model System for Reactions of Organic Molecules on Atmospheric Particles: SAMS and Ozone***, **D.J. Gaspar**,* Pacific Northwest National Laboratory*; T.M. McIntire,* University of California, Irvine*; A.S. Lea, N. Jaitly,* Pacific Northwest National Laboratory*; Y. Dubowski,* Technion-Israel Institute of Technology*; B.J. Finlayson-Pitts,* University of California, Irvine

Self-assembled monolayers (SAMS) provide a useful model system for the study of reactions of organic molecules. The preparation, use and analysis of SAMS are prone to variability and artifacts that can confound measurements that are do not provide molecular information on the state of the surface. Time of flight secondary ion mass spectrometry, on the other hand, provides a direct probe of the SAM surface chemistry. In this work, we describe our efforts to extract useful information regarding the reaction of ozone with saturated and unsaturated organic monolayers covalently bound to silicon dioxide surfaces under atmospherically relevant conditions. We have used a combination of imaging TOF-SIMS and spectral analysis aided by principal component analysis (PCA) to extract chemical information about the reaction of two model SAMS with ozone. The TOF-SIMS data provide the molecular information necessary to accurately interpret data obtained using other methods and described herein, including atomic force microscopy (AFM), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), and scanning Auger microscopy (AES). We show that the organic monolayer is removed from the Si substrate by ozone for an unsaturated 1-octene (C8=) monolayer, while it remains intact for a saturated dodecane (C12) monolayer. The implications of these observations for the atmospheric chemistry of organic molecules are discussed.

2:20pm **AS-WeA2 Formation and Volatilization of Small Molecules From a PTFE Matrix Upon MeV Alpha Particle Irradiation Examined by ToF-SIMS, SEM, and RGA***, **G.L. Fisher**, R.E. Lakis, C.C. Davis, C.J. Wetteland,* Los Alamos National Laboratory*; C.W. Szakal, N. Winograd,* Pennsylvania State University

The chemical structure and morphology at the surface of @alpha@-irradiated polytetrafluoroethylene (PTFE) has been examined and compared to unirradiated PTFE. The samples were irradiated to doses of 10@super 7@ to 10@super 11@ Rad using 5.5 MeV [@super 4@He]@super 2+@ from a tandem accelerator beam line. Static time-of-flight SIMS (ToF-SIMS), using a 20 keV C@sub 60@@super +@ source, was employed to probe chemical changes versus irradiation. Chemical images and high resolution spectra in both positive and negative polarity were collected and analyzed to reveal the effects of @alpha@ particle radiation on the chemical structure. Where appropriate, comparison is made to static ToF-SIMS data collected using a 15 keV Ga@super +@ primary ion source. Residual gas analysis (RGA) was utilized to monitor the evolution of volatile species during vacuum irradiation of the samples. Secondary electron microscopy (SEM) was used to observe the morphological variation of samples with increasing @alpha@ particle dose. The data show that PTFE nominally retains its chemical structure and morphology at @alpha@ doses @<=@10@super 9@ Rad; however, at @alpha@ doses @>=@10@super 10@ Rad the PTFE matrix suffers severe chemical degradation, morphological roughening, and material loss. Chemical degradation is evidenced in the ToF-SIMS spectra by fragmentation, unsaturation, and speciation of molecules in the PTFE matrix. ToF-SIMS images support the assertion that chemical degradation is the result of @alpha@ particle irradiation and show morphological roughening of the sample with increased @alpha@ dose. High resolution SEM images more clearly illustrate morphological roughening and the mass loss that accompanies high doses of @alpha@ particles. Finally, RGA confirms the supposition that the product of chemical degradation in the PTFE matrix with continuing irradiation is evolution of volatile species resulting in morphological roughening and mass loss.

2:40pm **AS-WeA3 Depth Profiling Analysis by Secondary Ion Mass Spectrometry: Historical Perspective and Current State-of-the-Art***, **C.W. Magee**,* Evans East **INVITED**

Secondary ion mass spectrometry has been used for in-depth characterization of materials and process for over 30 years. This talk will first touch briefly on history of SIMS depth profiling and then will review current state-of-the-art examples in semiconductors materials as well as in other areas as diverse from IC chips as potato chip bags and, yes, even the kitchen sink. Semiconductor areas will include, among others: profiling of ion implants with energies of a few hundred eV to a few million eV, along with high precision dose determination; and analyses of dopants and matrix elements in areas only a few 10's of um@super 2@. In addition, the talk will illustrate the utility of backside polishing for sample preparation.

3:20pm **AS-WeA5 SIMS Depth Profiling of Deuterium Labeled Polymers in Polymer Films and Multilayers***, **S.E. Harton**, F.A. Stevie, D.P. Griffis, H. Ade,* North Carolina State University

Thin planar polymer films are model systems for probing physical phenomena related to molecular confinement at polymer surfaces and polymer-polymer interfaces. Secondary Ion Mass Spectrometry (SIMS) can provide real-space depth profiles of tracer labeled polymers directly with sufficient depth resolution for optimal analysis of these systems. Three different bilayer systems have been used to investigate various physical phenomena at polymer-polymer interfaces, including reactive compatibilization and interfacial segregation. Deuterated polystyrene (dPS) has been employed as the tracer polymer and has been imbedded in a matrix of either unlabeled polystyrene (PS) or poly(cyclohexyl methacrylate) (PCHMA). Using selective solvents and a direct casting method, these doped films have been placed on either poly(methyl methacrylate) (PMMA) or poly(2-vinyl pyridine) (P2VP) and thermally annealed. X-ray specular reflectivity measurements confirm ultra-sharp interfaces between the two polymers using this preparation method, allowing for maximum depth resolution during SIMS analysis. Varied analysis conditions for a magnetic sector instrument (CAMECA IMS-6f) were used to optimize the depth resolution and sensitivity while minimizing matrix effects and sample charging. For all systems Cs+ and O2+ have been used as the primary ion source, with detection of negative and positive secondary ions, respectively. Impact energy and primary ion species have been shown to affect matrix ion count rate for the various films studied. Conditions required to achieve constant matrix secondary ion yield across the heterogeneous interface are discussed.

3:40pm **AS-WeA6 Adjacent Electron Beam Method for SIMS Analysis of Insulators at High Depth Resolution Conditions Using a Magnetic Sector Instrument***, C. Gu, Z. Zhu, **F.A. Stevie**, D.P. Griffis,* North Carolina State University

The adjacent electron beam charge neutralization method@footnote 1@ provides sufficient and self regulating charge neutralization for positive secondary ion SIMS analysis of both bulk and thick layer insulators using a magnetic sector instrument. This charge neutralization method has been extended to low primary ion impact energies, thus providing the ability to obtain high depth resolution SIMS analysis of both bulk and thick film insulating materials at high mass resolution. Results have been achieved with O@sub 2@@super +@ impact energy of 1.25keV and electron impact energy of 2.75keV. All prior analyses had been made using 5.5keV for O@sub 2@@super +@ and 6.5keV electron energy. Charge neutralization has been achieved for SiO@sub 2@, AlN, and AlGaN samples. Profiles have been obtained through at least two micrometers of insulator under the low impact energy conditions. While being able to profile through thick films is important, the real significance in these results is the ability to provide high depth resolution SIMS analysis of insulating materials. Electron impact charge neutralization using the adjacent electron beam method has been achieved with the following metal coatings: Al, Au, Ru, and Ir. Results will be presented demonstrating this method for both bulk and thick film insulating materials and current understanding of the mechanisms involved in this method of self regulating charge neutralization will be discussed. @FootnoteText@ @footnote 1@ A. L. Pivovarov, F. A. Stevie, and D. P. Griffis, SIMS XIV Proceedings, Applied Surface Science 231-232, 786-790 (2004).

4:00pm **AS-WeA7 The Atomic Motions behind Cluster Bombardment Secondary Ion Mass Spectrometry***, **B.J. Garrison**,* Penn State University **INVITED**

The advent of cluster ion sources for Secondary Ion Mass Spectrometry (SIMS) has opened new applications for this technique. In particular, the C@super 60+@ ion beam appears to be quite promising as a source for imaging and depth profiling of molecular substrates. From a fundamental point of view, the obvious question is what are the atomic motions that result from the cluster vs. atomic bombardment? Using molecular dynamics computer simulations we have begun to elucidate the basics mechanisms of ejection or sputtering due to C@super 60@ bombardment of solids. Systems investigated to date include a clean Ag substrate,@footnote 1@ a thin film of benzene on Ag@footnote 2@ and water ice. The various systems investigated to date will be discussed along with relevant experimental data. @FootnoteText@ @footnote 1@ Enhancement of Sputtering Yields due to C@super 60@ vs. Ga Bombardment of Ag{111} as Explored by Molecular Dynamics Simulations, Z. Postawa, B. Czerwinski, M. Szewczyk, E. J. Smiley, N. Winograd and B. J. Garrison, Analytical Chemistry, 75, 4402-4407 (2003)@footnote 2@ Microscopic Insights into the Sputtering of Ag{111} Induced by C60 and Ga Bombardment of Ag{111}, Z. Postawa, B. Czerwinski, M. Szewczyk, E. J. Smiley, N. Winograd and B. J. Garrison, J. Phys. Chem. B, 108, 7831-7838 (2004) .

4:40pm **AS-WeA9 Comparison of TOF-SIMS and XPS Analysis Using a C@sub 60@ Ion Sputter Cleaning***, **N. Sanada**, T. Miyayama, J.S. Hammond,* ULVAC-PHI, Inc., Japan*; J.F. Moulder, S.R. Bryan,* Physical Electronics

The analysis of chemical layers buried in the near surface region from 1 to 100 nm is of great interest to polymer and biomaterials scientists. However, it has been a great challenge to get chemical information from this region of some materials because of chemical damage observed following ion beam sputtering. Recently, we have applied a buckminsterfullerene (C@sub 60@) ion beam for sputter cleaning and depth profiling to minimize chemical damage for organic and inorganic materials.@footnote 1@ Extremely low sputtering degradation of many organic materials such as polytetrafluoroethylene,@footnote 1@ polyesters, gelatins, and multilayer latex materials@footnote 2@ were observed by XPS. The effects of different C@sub 60@ ion beam accelerating voltages and impact angles on accumulation of residual carbon and chemical damage were examined with XPS using standard samples of polyethyleneterephthalate (PET) and SiO@sub 2@. The quantities of carbon residue in the SiO@sub 2@ film reduced as the increasing accelerating voltages. The impact angle of the ion beam also affected the carbon residue in the film.@footnote 3@ Based on these experiments, an optimized protocol for using a C@sub 60@ ion beam with XPS was developed. We will discuss TOF-SIMS analysis of polymers after sputter cleaning with a C@sub 60@ ion beam under the protocol optimized with XPS. For many polymers, the high energy resolution XPS spectra following C@sub 60@ ion beam exposure showed a constant elemental and functional group stochiometry. The higher sensitivity of TOF-SIMS analysis of these materials allows an examination of more subtle changes induced by the C@sub 60@ ion beam not observed in the XPS analysis. @FootnoteText@ @footnote 1@ N. Sanada et al., Surf. Interface Anal., 36 (2004) 280.@footnote 2@ D. Sakai, et al., J. Surf. Anal. (Tokyo), submitted.@footnote 3@ N. Sanada, et al., AVS 51st. Int. Symp. As-TuM5.

5:00pm **AS-WeA10 TOF-SIMS Imaging of OLED Devices using a Au Cluster Ion Beam***, **S.R. Bryan**,* Physical Electronics*; J.S. Hammond, N. Sekiya, A. Yamamoto,* ULVAC-PHI, Inc.

Organic light emitting diode (OLED) technology is a growing research area which may lead to next generation display and lighting commercial products. OLED is based on the use of multi-layers of thin molecular or polymer materials which emit light directly when a voltage is applied. The total thickness of the multi-layer film structure is usually less than 500nm. The organic layers can be doped with specific enhancing molecules to get the desired brightness and color. This new cutting edge technology based on patterned organics requires analytical techniques that can characterize the organic structure of the devices with submicron spatial resolution and good depth resolution. TOF-SIMS offers one of the only techniques that can provide the needed spatial resolution with molecular specificity. One of the most important commercial developments in TOF-SIMS instrumentation in recent years has been the introduction of cluster ion beams for enhancement of organic molecular secondary ion yields. Although Ga+ LMIG sources, which have been used in TOF-SIMS since 1990, has sufficient spatial resolution for most applications, the secondary ion yield of organic molecules from Ga+ sputtering is insufficient for many applications. Development of the Au LMIG emitter, which allows TOF-SIMS analysis with Au+, Au2+ or Au3+, extends the capabilities of TOF-SIMS to image patterned organic materials. The capabilities of imaging with the Au LMIG emitter will be compared to the Ga emitter for characterization of OLED devices. Spatial resolution, damage cross-sections, and ultimate detection limits will be compared between Ga, Au, Au2, and Au3 for typical molecules used in OLED devices.

Biomaterial Interfaces
Room 311 - Session BI1-WeA
Protein-Surface Interactions

Moderator: J.Y. Wong, Boston University

2:00pm **BI1-WeA1 Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) of Short Peptides-Noble Metal Surface Interactions Analyzed by Principal Component Analysis (PCA)***, **N. Suzuki**, L.J. Gamble, D.G. Castner, M. Sarikaya, F.S. Ohuchi,* University of Washington

Recent progress in the adaptation of combinatorial biology selection protocols to materials science has created a new class of polypeptides with specific affinity to inorganics. Here, we have used short peptide chains whose sequence consists of MHGKTQATSGTIQS in single- and triple-repeat forms, and have assessed quantitatively their binding specificity to Au, Ag and Pd surfaces by Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS). Due to high mass resolutions, ToF-SIMS is capable of providing information about specific amino acidsâ?"surface interactions as well as their mutual interactions at the surface, but numerous mass fragments from the amino acids complete the analysis. We have therefore adopted Principal Component Analysis (PCA) to the static ToF-SIMS spectra, from which characteristic information related to binding specificity was obtained by reducing the dimension of data sets. The score plot in the PCA analysis has revealed that the effect of alkali ions from buffer solution significantly alters the fragmentation patters. Once, the grouping based on alkali ions content is carried out, the loading plot within the same group suggests that the strength of a localized amino acid sequence, MHGK, observed from the triple repeated chain differentiates the binding characteristics specific to a certain type of inorganics. In addition, the inherent binding site of this peptide toward inorganics is determined from loading plots. This technique is capable of analyzing the complex, multivariate ToF-SIMS spectra from the adsorbed polypeptide films and compared to univariate methods providing unique insight about the sample.

2:20pm **BI1-WeA2 The Application of Magnetic Tweezers to High Throughput Screening of Peptide Libraries***, **H. Shang**, G.U. Lee,* Purdue University

Single molecule force measurement techniques, such as, the atomic force microscope (AFM), have provided us with the ability to directly measuring the force and displacement involved in the rupture single ligand-receptor interactions. These techniques are providing us with fundamentally new information about molecular recognition interactions, which potentially is extremely useful for designing ligands for specific receptors. Magnetic tweezers is a technique in which micron size paramagnetic particles are used to transduce pico-newton scale force to single ligand-receptor pairs. This technique has the force resolution of a single hydrogen bond and allows millions of ligand-receptor pairs to be simultaneously screened. A kinetic model is used to analyze the data and the binding affinities of different ligand-receptor pairs are revealed by statistical analysis. The advantage of using this technique over conventional assays is that force can be used to define the affinity of the bond. In this presentation, we review recent single molecule force measurements with AFM and advances that have been made in screen phage libraries using magnetic tweezers.

2:40pm **BI1-WeA3 Invited Paper***, **M. Grinstaff**,* Boston University **INVITED**

NO ABSTRACT SUBMITTED.

Biomaterial Interfaces
Room 311a - Session BI2-WeA
Cell-Surface Interactions

Moderator: J.Y. Wong, Boston University

3:20pm **BI2-WeA5 Receptor-Ligand Interactions to Promote Endothelial Cell Adhesion and Function***, **G.A. Truskey**, W.M. Reichert, B. Chan,* Duke University **INVITED**

Endothelial cell adhesion and proper function are crucial for the development of tissue-engineered vessels and non-thrombogenic vascular grafts. In vivo shear stresses and mechanical forces can reduce adhesion endothelial cell function. We have systematically examined factors affecting endothelial adhesion and identified. To promote rapid and firm adhesion we developed a dual ligand system using a high affinity ligand to initiate adhesion and facilitate integrin-mediated adhesion. Avidin was used as the high affinity ligand. This ligand-receptor pair enabled endothelium to resist high shear stresses encountered in vivo. An RGD group was grafted onto avidin to permit adhesion to integrins. Interestingly, the RGD-avidin bound the endothelium in solution with high affinity and served to prime adhesion once the cells attached. Functional studies indicated that this dual ligand system promoted a nonthrombogenic phenotype. Preliminary in vivo studies of endothelium attached to ePTFE grafts indicate that the dual ligand system can promote firm adhesion but mechanical trauma to the graft is a significant limitation to complete coverage of endothelium. Current work is optimizing endothelial attachment to commercially available grafts and identifying a tissue-engineering alternative for endothelialization. (supported by NIH grants RO1 HL44972 and R21 HL72189.).

4:00pm **BI2-WeA7 Interactions Between Membrane-Bound Receptors and Soluble Ligands Measured by AFM, QCM-D and SPR***, **Y. Lam**, S.M. Alam, S. Zauscher,* Duke University

Many proteins in the immune system are membrane bound, presented on the cell surface. Once bound to their soluble ligands, they facilitate interactions to initiate a foreign body response. To gain a deeper understanding of these interactions we initially investigated the bonds between soluble antigen and antibodies by single molecule force spectroscopy using an atomic force microscope (AFM). We immobilized monoclonal antibodies (mAb A32) specific to HIV-1 envelope glycoprotein gp120 on a substrate, and incubated this surface with gp120. This interaction between gp120 and mAb A32 causes a conformational change in gp120, exposing an epitope for a secondary mAb (17b) to bind. We measured the strength of interaction between gp120 and 17b by single molecule force spectroscopy using a cantilever tip decorated with 17b. AFM was also used to generate an energetic landscape of the binding pocket via pulling force experiments at different pulling rates. We also report on our measurements using membrane bound receptors, providing a more native environment for the system. Quartz crystal microbalance with dissipation (QCM-D) was employed to monitor the formation of protein-lipid bilayer constructs. Finally we report on measurements using surface plasmon resonance (SPR) to elucidate changes in affinity between membrane bound and immobilized soluble receptors. This detailed knowledge of receptor ligand interactions is essential to better engineer and tailor therapeutic treatments for various diseases.

4:20pm **BI2-WeA8 A Photolithographic Method for Patterning Soft Polyacrylamide to Enhance Smooth Muscle Cell Elongation***, **J.G. Jacot**, J.L. Jackel, S.G. Koester, J.Y. Wong,* Boston University

Vascular smooth muscle cells (VSMCs) express a contractile phenotype in vivo that is lost as cells proliferate in vitro. The manufacture of a successful tissue engineered blood vessel requires the ability of VSMCs to proliferate and populate a scaffold, then revert to a contractile state. In vivo, VSMCs are highly elongated and previous studies from our lab have shown that cell shape influences the localization of proteins such as F-actin and calponin that have a contractile function. Further studies by others found that cell constrainment can also reduce proliferation. However, all these studies investigated cells on rigid substrates, which do not mimic the mechanical environment of the arterial wall, and cannot functionally measure contractile force generation. We have developed a soft lithography technique for patterning 10-micron lanes of collagen on soft polyacrylamide hydrogels. These patterned materials allow separate control of substrate elasticity and cell shape and also allow measurement of cell-generated forces by following the displacement of embedded fluorescent marker beads. Because these materials are fully hydrated and very compliant compared to previously patterned rigid cell culture substrates, maintaining high pattern resolution is difficult. The 10-micron patterns presented here are higher resolution than previously published protein patterns on soft polyacrylamide. Passaged bovine arterial VSMCs plated on these patterned hydrogels attach and spread only on the collagen lanes and have aspect ratios 2-fold higher than unpatterned VSMCs.

4:40pm **BI2-WeA9 Identification of Residual ECM Proteins Retained at pNIPAM Surfaces using Time-of-Flight SIMS***, **H.E. Canavan**, M. Greenfeld, X. Cheng, D.J. Graham, B.D. Ratner, D.G. Castner,* University of Washington

Treatment of tissue culture polystyrene (TCPS) with poly(N-isopropyl acrylamide) (pNIPAM) has been developed as a technique for the harvest of intact cell layers. Recently, we demonstrated that although low-temperature liftoff removes the majority of the Extracellular Matrix (ECM) concurrently with the cells, some protein does remain at the pNIPAM surface. However, little is known about the identity of the ECM proteins retained at the pNIPAM surface after cell liftoff. In this work, we characterized the time-of-flight secondary ion mass spectrometry (ToF-SIMS) molecular fragmentation pattern of adsorbed single protein mixtures of important ECM proteins (e.g., laminin, fibronectin, and collagen). We next performed Principal Component Analysis (PCA) to distinguish between the proteins through the identification of unique amino acid fragmentation patterns in the ToF-SIMS positive ion spectra, a technique previously developed in our group. In this way, a model ToF-SIMS projection of the ECM was constructed. We subsequently compared the ToF-SIMS fragmentation pattern of the proteinaceous layer retained on the pNIPAM surface to that of the model ECM. ToF-SIMS fragmentation patterns of bovine serum albumin and serum-containing media controls were compared as positive controls as well. Using the comparison of the model ECM to that of ECM retained on pNIPAM surfaces, we discuss the identity of the proteins retained on the substrate after low-temperature liftoff from pNIPAM surfaces. We then compare our results to those obtained from analysis of the ECM using other surface analytical techniques, including immunoassay, gel electrophoresis, and matrix-assisted laser desorption ionization (MALDI).

5:00pm **BI2-WeA10 Compartmentalized Bioreactor Mitigates Culture Shock-Engenders Bone Tissue from Isolated Bone Cells***, **D. Ravi**, E.A. Vogler,* Penn State University

Reducing the profound gap between the physiological environment of the bone cells and in vitro cell culture models is critical for realizing the promise of tissue-engineering strategies to replace, regenerate and restore function to bone lost as a result of disease or injury. An advanced bioreactor that mitigates culture shock or the behavioral variations associated with the transition of bone cells from the in vivo to the in vitro environment was developed and tested. The bioreactor based on the principle of simultaneous-cell-growth-and-dialysis, separates a cell growth chamber from a media reservoir by a dialysis membrane, compartmentalizing cell growth and cell nutrition functions. As a consequence of compartmentalization, the pericellular environment is unperturbed by continuous perfusion or punctuated re-feeding schedules and luxury macromolecules synthesized by cells are retained in a manner that more closely simulates the in vivo condition. The stable culture conditions afforded by the bioreactor sustained model cell lines, mouse calvaria-derived MC3T3-E1 (ATCC CRL-2593) and human fetal osteoblasts (hFOB 1.19, ATCC CRL-11372) for extended time periods (30-120 days) without the need for sub-culture. The transformation of isolated osteoblast inoculum to mineralized, collagenous tissue that simulates native osteoid was followed using optical microscopy and scanning and transmission electron microscopy. Mineralization was assessed using Von Kossa assay and SEM-EDS (Energy Dispersive Spectroscopy. Development of differentiated, collagenous bone tissue (biosynthetic osteoid) from disaggregated osteogenic cells over 120 day culture was demonstrated on both 2-D polymer substrates as well as 3-D hydroxyapatite scaffolds. The compartmentalized bioreactor substantially mitigates culture shock and shows promise as an ideal in vitro tool for evaluation of orthopedic biomaterials and development of engineered bone tissue.

Electronic Materials and Processing
Room 309 - Session EM-WeA

Contacts to Semiconductors

Moderator: S.E. Mohney, The Pennsylvania State University

2:00pm **EM-WeA1 Effect of Si on the Ohmic Behavior of Ti/Al/Mo/Au Metallization for AlGaN/GaN HEMTs***, **F.M. Mohammed**, L. Wang, H.J. Koo, I. Adesida,* University of Illinois at Urbana-Champaign

The high breakdown voltage and high saturation current of AlGaN/GaN HEMTs present great potential for applications in power amplification. High performance devices for such application require low parasitic ohmic contact resistance. We present an investigation on the study of the effects of Si incorporation in Ti/Al/Mo/Au metallization scheme. Si is a commonly used n-type dopant in GaN alloys systems, and implantation and diffusion doping are utilized to increase carrier concentration at the surface of epilayers. In Ti/Si-based contact metallizations, the formation of TiSi@sub x@ at the interface is believed to lower the barrier height for conduction of current across the metal/GaN junction. In this study, we have carried out experiments to optimize the thicknesses of Si introduced in the metallization scheme. Impact of the place of insertion within the metallization scheme (e.g. Ti/Si/Al/Mo/Au vs. Ti/Si/Al/Si/Mo/Au) has also been studied. Si incorporation, surface treatment, and annealing are collectively optimized to induce a reduction in contact resistance. An example is the optimized Ti/Si/Al/Si/Mo/Au metallisation annealed at 850

@super o@C for which a contact resistance (R@sub c@) and specific contact resistivity (@rho@@sub c@) as low as 0.16 ± 0.02 @OMEGA@.mm and 6.77 ± 0.7 x 10@super -7@ @OMEGA@.cm@super 2@ were obtained, respectively. This represents a significant reduction when compared to what was correspondingly obtained for Ti/Al/Mo/Au at 0.41 @OMEGA@.mm and 4.78 x 10@super -6@ @OMEGA@.cm@super 2@, respectively. Atomic force microscopy (AFM) and Auger electron spectroscopy (AES) characterization are utilized to reveal the nature of ohmic contact formation and the evolution in surface morphologies of the metallization schemes and epilayers.

2:20pm **EM-WeA2 Non-uniform Interfacial Reactions of Ti/Al/Mo/Au Ohmic Contacts on n-AlGaN/GaN Heterostructure and its Effect on Carrier Transport***, **L. Wang**, F.M. Mohammed, I. Adesida,* University of Illinois at Urbana-Champaign

Ti/Al/Mo/Au multilayer metallization scheme has been demonstrated to have low ohmic contact resistance, high thermal stability, and sharp edge acuity on AlGaN/GaN high electron mobility transistors (HEMT). Transmission electron microscopy (TEM) is used to elucidate the cross-sectional interfacial microstructure and to gain insight into the formation mechanism of low-resistance ohmic contacts. It has been observed that reactions between the metallization and the AlGaN layer did not proceed uniformly. Localized penetration through AlGaN layer up to a depth of 130 nm was observed. Thinning of the AlGaN layer was noted where there was no penetration. Energy dispersive x-ray spectroscopy (EDS), and high resolution TEM (HRTEM) analysis confirmed that the reaction products were TiN. A strong correlation between the appearance of TiN islands and threading dislocations in the epitaxial layers was observed. Further analysis indicated that threading dislocations served as short-circuit diffusion channels, and thus are responsible for the non-uniform reaction. TiN islands have a large total area of intimate contact with the two-dimensional electron gas (2DEG), and since no tunneling of electron through the AlGaN is required, a low resistance ohmic contact is obtained. Methods for promoting and controlling the non-uniform interfacial reaction are proposed.

2:40pm **EM-WeA3 Polarization-enhanced Ohmic Contacts to GaInN-based Blue Light-Emitting Diodes***, **T. Gessmann**, Y.A. Xi, H. Luo, J.K. Kim, J.Q. Xi, K. Chen, E.F. Schubert,* Rensselaer Polytechnic Institute

Thin p-type Ga@sub 1-x@In@sub x@N cap layers have been grown on p-type GaN contact layers of blue light emitting diodes (LEDs) using metal-organic vapor phase epitaxy (MOVPE) with an AIX 200/4 RF-S reactor. The Ga@sub 1-x@In@sub x@N cap layers have thicknesses smaller than 4 nm and In-contents varying between x = 0.1 and 0.2. The LED structure consists of a GaN nucleation layer grown on c-oriented sapphire, a 2 µm-thick n-type GaN layer, 5 Ga@sub 0.86@In@sub 0.14@N quantum wells embedded in GaN-barriers, and a 0.2 µm-thick p-type GaN layer. Having a cap layer thickness below the critical thickness of Ga@sub 1-x@In@sub x@N on GaN, a piezoelectric field will be present in the cap layer resulting in increased carrier tunneling probabilities through the metal-semiconductor barrier. The In-content and the strain status of the cap layers have been analyzed using HR X-Ray diffractometry. For cap layer thicknesses smaller than 4 nm, pseudomorphic Ga@sub 1-x@In@sub x@N has been obtained for three different In-contents x = 0.1, 0.15 and 0.2. LEDs have been fabricated using standard photolithograpy processes, CAIBE mesa etching and electron beam deposition of Ni/Au and Ti/Al/Ni/Au contact metals. The specific contact resistance, diode series resistance, ideality factor and optical output power of the LEDs are determined and compared to devices without capping layer. A specific contact resistance @rho@@sub c@ = 1.8 x 10@super -4@ @Ohm@ cm@super 2@ has been obtained for samples with InGaN cap layer; this value is significantly smaller than @rho@@sub c@ of a sample without cap layer. The results will be discussed in terms of a model relating the cap layer thickness and In-content to the p-type contact resistance.

3:00pm **EM-WeA4 Indium-based Ohmic Contacts to n-GaSb and the Influence of Surface Passivation***, **J.A. Robinson**, S.E. Mohney,* The Pennsylvania State University

Gallium antimonide and related ternary and quaternary semiconductors have shown great potential for electronic devices as well as optoelectronic devices in the 0.3 - 8 µm wavelength range. High quality ohmic contacts help ensure device reliability and improve performance by providing a low resistance, a uniform interface morphology, and minimal semiconductor consumption. Pd-based contacts to n-GaSb that do not include In provide specific contact resistance values as low as 5 x 10@super -6@ @Omega@-cm@super 2@. However, by adding In, the specific contact resistance is reduced by 80%. We present two high quality In-based contacts that include Pd. Initial experiments included a Pd/In/Pd/Pt/Au contact that provides a specific contact resistance of 1.8 x 10@super -6@ @Omega@-cm@super 2@ using a modified pre-metallization surface treatment that involves 2.1% (NH@sub 4@)@sub 2@S. However, the surface and interfacial reaction morphology of the Pd/In/Pd/Pt/Au contact was less than optimal. As a result, sputtered Pd@sub 3@In@sub 7@/X/Au (X = Pt,W,WSi@sub 2@, or WSiN) contacts were explored as a means to improve reaction morphology and thermal stability. Contacts utilizing WSiN provide a specific contact resistance of approximately 3 x 10@super -6@ @Omega@-cm@super 2@ using a conventional surface treatment, and 1.8 x 10@super -6@ @Omega@-cm@super 2@ when the modified surface treatment is used. While the Pd@sub 3@In@sub 7@/WSiN/Au contact provides specific contact resistance values comparable to the best reported In-based contacts, this contact exhibits an improved reaction morphology and better thermal stability compared to other contacts.

3:20pm **EM-WeA5 Controlling Interfacial Reactions in Ferromagnetic Metal / GaAs Heterostructures***, **B.D. Schultz**,* University of Minnesota **INVITED**

Growth of epitaxial ferromagnetic metal contacts on compound semiconductors with atomically abrupt interfaces is often a challenge due to thermodynamic instabilities at the interface between the two materials and the subsequent formation of solid state reaction products. Elemental ferromagnetic metals, such as Fe and Co, can be grown by molecular-beam epitaxy (MBE) as single crystal films on GaAs; however, they are not thermodynamically stable and reacted phases form at the interface. The initial nucleation of Fe on GaAs surfaces is strongly influenced by the GaAs surface reconstruction, but results in little disruption of the reconstruction itself. Fe/GaAs reactions are reduced at lower MBE growth temperatures with a reacted layer thickness of approximately three monolayers at 15°C. Post-growth anneals at 250°C do not result in the reaction of additional GaAs, but the anneals significantly alter the electronic properties of the interface. Co is more reactive than Fe on GaAs and forms a reaction region composed of Co@sub 2@GaAs, CoGa, and CoAs. Thermodynamically stable metals such as ErAs can be used as epitaxial diffusion barriers to minimize Fe-Ga-As and Co-Ga-As interfacial reactions for growth temperatures as high as 225°C. This paper will emphasize the correlation between the structure, chemistry, magnetism and transport properties of Fe@sub x@Co@sub 1-x@/GaAs and Fe@sub x@Co@sub 1-x@/ErAs/GaAs contacts as determined by STM, RHEED, LEED, XPS, RBS, XRD and TEM. Supported by: ONR, DARPA, NSF/DMR, and AFOSR.

4:00pm **EM-WeA7 Molecular Beam Epitaxial Growth of Sc@sub x@Er@sub 1-x@Sb on III-V Compound Semiconductors***, **S.G. Choi**,* Univerrsity of Minnesota*; B.D. Schultz, C.J. Palmstrom,* University of Minnesota

Epitaxial metallic or semimetallic layers in semiconductors have potential application in novel electronic devices. Rare-earth group-V (RE-V) compounds have received much attention since they are thermodynamically stable and epitaxial on III-V semiconductors. In particular, Sc@sub y@Er@sub 1-y@As alloys have been employed successfully in GaAs-based materials, however, application of Sc@sub y@Er@sub 1-y@As alloys to other III-V's has been less fruitful due to large lattice-mismatches. Therefore, RE-V alloys with lattice parameters close to InP or GaSb are of considerable interest and Sc@sub x@Er@sub 1-x@Sb is one of the promising candidates. The lattice parameter of Sc@sub x@Er@sub 1-x@Sb ranges from 5.85Å (ScSb) to 6.11Å (ErSb), and can therefore be lattice-matched to InP, InAs, and GaSb by controlling the Sc to Er ratio. In this work, Sc@sub x@Er@sub 1-x@Sb alloys have been grown on various III-V semiconductors by molecular beam epitaxy (MBE). The surface ordering was monitored in-situ by RHEED and LEED. ErSb grown on GaSb(100) exhibited a (1x1) surface ordering with high Sb incorporation and a mixed (1x4)/(4x1) with low Sb incorporation. In-situ XPS data showed no significant differences in Er and Sb coverage between the two surfaces, however, the amount of Ga riding on the two surfaces was different, which may cause the different surface ordering. One possible mechanism for Ga atoms to segregate on a 500Å-thick ErSb film can be explained in terms of an embedded growth model. Growth of Sc@sub x@Er@sub 1-x@Sb on InAs and InP is more challenging since intermixing of the different group-V elements at the interface would be expected to degrade the quality of interface. Different methods for minimizing the intermixing at the interface will be discussed. Supported by ONR, DARPA, and ARO.

4:20pm **EM-WeA8 Chemically-Induced Point Defects and Schottky Barrier Formation at Metal/4H-SiC Interfaces***, **L.J. Brillson**, S. Tumakha, M. Gao,* The Ohio State University*; S. Tsukimoto, M. Murakami,* Kyoto University, Japan*; D.J. Ewing, L. Porter,* Carnegie Mellon University

We have used depth-resolved cathodoluminescence and Auger electron spectroscopies, DRCLS and AES, respectively, to determine the role of chemically-induced defects on 4H-SiC barrier formation on a nanometer scale. DRCLS of 5 nm Au, Ag, Ti, and Ni overlayers reveal formation of mid-gap defect transitions at ~1.8 eV and 2.85 eV extending only nanometers away from the junction. These states vary in their ranges of depth and depend sensitively on interface reactivity and subsequent UHV annealing. Their pervasive appearance near morphological defects and the absence of new gap states indicates that native defects rather than metal-specific states produce the dominant interface levels. For thicker TiAl Ohmic contacts with 5 min 1000 C anneals, cross-sectional scanning electron microscopy, AES, and DRCLS reveal a continuous ternary Ti-Si-C interfacial layer ~100 nm thick, a 1.9 eV sub-band gap transition localized within this depth and a 2.8 eV emission extending into the SiC, indicating both reaction-induced compound and defect formation, respectively. Within annealed NiTiAl Ohmic contacts, Ni silicide and Ti carbide form with a qualitatively different ~ 1.6 eV transition extending beyond the reaction zone. AES showing C movement from SiC into the metal overlayer indicate formation of a C-deficient SiC point defect. Thus the major difference in TiAl and NiTiAl interfacial reactions induces different interfacial gap states. For Ni/SiC reacted diodes, DRCLS and current-voltage measurements show a close correspondence between the Schottky barriers and deep level defect energies from diode to diode. Furthermore, the range of energies bounded by these defects corresponds with Schottky barrier heights reported previously via electrical measurements. This correspondence between chemically-induced deep levels at bulk defect energies and the range of macroscopic Schottky barriers for SiC appears to be a more general phenomenon, extending to other compound semiconductors as well.

4:40pm **EM-WeA9 Metal Germanide Schottky Contacts to Relaxed and Strained Germanium***, **A. Khakifirooz**, O.M. Nayfeh, M.L. Lee, E. Fitzgerald, D.A. Antoniadis,* Massachusetts Institute of Technology

Significant mobility enhancement offered by germanium channel MOSFETs and especially strained-Ge devices makes them very attractive for the deca-nanometer transistor scaling. A low resistivity contact to the S/D junctions is, however, the key to successful integration of such devices. Since high doping levels are difficult to achieve in Ge, Schottky S/D MOSFET is considered as an interesting option that also relaxes the constraints on the S/D junction abruptness. A systematic study of the formation of different metal germanide phases has been recently performed and they were characterized in terms of their electrical resistivity.@footnote 1@ In this work we study the Schottky barrier formed between germanium and Ni, Pd, and Pt germanides that were previously identified as the low-resistivity phases and offer a relatively wide processing window. Metal germanide is formed by annealing a very thin layer of metal (~15 nm) deposited onto HF-last Ge samples and patterned by lift-off. Samples are annealed in a furnace for 15 min. or in an RTA chamber for 1 min at different temperatures in the range of 350-500°C. Some diodes are also fabricated on strained Ge epitaxially grown on relaxed Si@sub 0.4@Ge@sub 0.6@ buffer with an ultrathin silicon cap. In this case, the metal thickness is selected in a way to consume the Si cap and almost the entire strained-Ge layer without touching the SiGe buffer layer to avoid excessive leakage. XRD and XTEM analysis are performed to study the crystallinity and morphology of the germanide layers, whereas I-V and C-V measurements are used to characterize the Schottky barrier. While nearly ideal barriers (ideality factor as good as 1.01), with a barrier height of 0.55-0.57 eV are obtained on bulk germanium, diodes fabricated on strained-Ge samples show excessive leakage current and high ideality factor (~1.8). Possible mechanisms responsible for this non-ideality are discussed. @FootnoteText@ @footnote 1@S. Gaudet et al., AVS 51st Int. Symp., 2004.

5:00pm **EM-WeA10 Ni Diffusion Studies From NiSi/Hf-based High-K Dielectric Stack Into Si***, **P. Zhao**, M.J. Kim, B.E. Gnade, R.M. Wallace,* University of Texas at Dallas

Fully silicided NiSi has been studied as a metal gate electrode due to low resistivity, scability and work function tunability.@footnote 1,2,3@ However, there remain many challenges for the integration of NiSi metal gates, such as phase stability, incomplete silicidation and possible Ni diffusion. The interdiffusion of Ni from NiSi through dielectrics into the underlying Si substrate (channel) has not yet been reported in the literature to our knowledge. We have investigated the Ni diffusion from NiSi through SiO@sub X@N@sub Y@ and Hf-based gate dielectrics into the Si channel. SIMS profiles show that interdiffusion of Ni from NiSi through a 13Å SiO@sub X@N@sub Y@ into the Si channel can be observed after thermal anneal budgets even as low as 350°C for 60min, representative of a typical backend process. It is also found that the Ni penetration increases with temperature and time. Although the penetration is reduced for a stack with thicker HfSiON dielectrics (23Å), the diffusion is observed when the stack is annealed for 60min at 400°C. Compared to N@sub 2@ annealing, deuterated forming gas annealing appears to enhance the Ni penetration. Both backside and front side SIMS, XRD, and HRTEM results will be presented. The possible diffusion mechanism will be discussed. This work is supported by Texas Instruments and the Semiconductor Research Corporation. @FootnoteText@ @footnote 1@ Z. Krivokapic, W. Maszara, F. Arsnia, E. Patron, Y. Kim, L. Washington, et al., VLSI 2003, p. 131-132 (2003)@footnote 2@ J. Kedzierski, E. Nowak, T. Kanarsky, Y. Zhang, D. Boyd, R. Carruthers, et al., IEDM 2002, p.247-250 (2002)@footnote 3@ C. Cabral, Jr., J. Kedzierski, B. Linder, S. Zafar, V. Narayanan, S. Fang, A. Steegen, P. Kozlowski, R. Carruthers, and R. Jammy. 2004 Symposium on VLSI Technology Digest of Technical Papers, p.184-185 .

Magnetic Interfaces and Nanostructures
Room 204 - Session MI+EM-WeA

Magnetic Semiconductors

Moderator: A.T. Hanbicki, Naval Research Laboratory

2:00pm **MI+EM-WeA1 Effects Limiting the Formation of Ferromagnetic III@sub 1-x@Mn@sub x@V Alloys by Epitaxial Growth***, **J.K. Furdyna**,* University of Notre Dame **INVITED**

III@sub 1-x@Mn@sub x@V alloys (e.g., Ga@sub 1-x@Mn@sub x@As), comprised of Mn@super +2@ incorporating substitutionally for the group-III element in the III-V lattice are captivating the attention of the scientific community worldwide because of the promise they hold for spin-electronic applications. Incorporation of Mn into the III-V lattice in sufficient concentrations to render the III@sub 1-x@Mn@sub x@V alloy ferromagnetic must be carried out by non-equilibrium low-temperature epitaxy, whereby Mn concentrations x approaching 0.10 can be attained. The ferromagnetism of these alloys occurs because, in addition to providing magnetic moments, the Mn ions also act as acceptors, thus supplying large concentrations of holes that mediate the ferromagnetic interaction between magnetic moments of the Mn ions. A mean field theory projects that the Curie temperature T@sub C@ should scale as the product of the Mn concentration x and of the hole density p. Thus, in principle, one should expect above-room-temperature ferromagnetism for large values of the x·p product. Our research on Ga@sub 1-x@Mn@sub x@As and In@sub 1-x@Mn@sub x@Sb has shown, however, that the Fermi energies achievable in these materials cannot exceed a certain maximum E@sub Fmax@, corresponding to a maximum hole concentrations p@sub max@. This occurs because the relationship between the creation energies for negatively-charged defects (such as the desired substitutional Mn acceptors Mn@sub III@, e.g. Mn@sub Ga@ or Mn@sub In@) and positively-charged defects (such as the unwanted interstitial Mn double donors, Mn@sub I@) is controlled by the Fermi energy. When E@sub F@ in the III@sub 1-x@Mn@sub x@V reaches E@sub Fmax@ due to the increasing free hole density, further formation of Mn@sub III@ becomes energetically unfavorable, and a high concentration of compensating Mn@sub I@ defects begins to form. The creation of Mn@sub I@ is deleterious to the ferromagnetism for multiple reasons: (1) compensation by the double Mn@sub I@ donors reduces the hole concentration, (2) interstitial Mn is RKKY-inactive (due to negligible p-d exchange), and (3) Mn@sub I@ forms antiferromagnetic pairs with Mn@sub III@, reducing further the density of Mn ions that contribute to the ferromagnetism of the III@sub 1-x@Mn@sub x@V alloy. Thus any increase of the Mn@sub I@ concentration automatically leads to lowering the value of T@sub C@. Ion-channeling experiments directly reveal this type of interstitial Mn creation whenever p approaches p@sub max@ due to a high Mn concentration. In this talk we concentrate on showing that substitutional vs. interstitial incorporation of Mn in III@sub 1-x@Mn@sub x@V alloys is determined by the Fermi level during the growth process itself, no matter what is the source of holes that establish the value of E@sub F@, and independent on the spatial location of the acceptors with respect to the magnetic Mn ions. To demonstrate this, we discuss two types of growth experiments that allowed us to vary the Fermi level independently of the Mn concentration, namely, experiments on Be co-doping of III@sub 1-x@Mn@sub x@V alloys; and on modulation doping of Al@sub 1-y@Ga@sub y@As/Ga@sub 1-x@Mn@sub x@As/Al@sub 1-y@Ga@sub y@As heterostructures by Be. Having established causes for the limit which nature imposes on incorporating substitutional Mn ions at the Group-III sites in III-Mn-V alloys, I will then discuss possible strategies for circumventing this obstacle, with an eye on increasing the Curie temperature of these novel ferromagnetic semiconductors.

2:40pm **MI+EM-WeA3 Structural Properties, Lattice Dynamics, and Optical Properties of GaMnN**, *W.E. Fenwick, M.H. Kane, M. Strassburg, A. Asghar, S. Gupta, H. Kang,* Georgia Institute of Technology*; Z. Hu,* Georgia State University*; S. Graham,* Georgia Institute of Technology*; U. Perera,* ***N. Dietz****,* Georgia State University*; I.T. Ferguson,* Georgia Institute of Technology

Dilute magnetic semiconductors (DMS) show promise as spintronic materials because of their electrical and magnetic properties. E.g., GaMnN exhibit ferromagnetism (FM) above room temperature (RT). Application of such materials for RT spintronic devices requires an understanding of the origin of this magnetism, which is still under debate in the literature. Knowledge of the structural properties is essential to determine the origin of the RT FM in GaMnN. Therefore this work provides structural and optical studies of GaMnN to reveal the crystalline quality, lattice dynamics, and some fundamental properties such as the optical constant. Increasing Mn concentration significantly affects long-range lattice ordering. The observation of a local vibrational Raman mode at 669 cm@super -1@ combined with the slight excess of metal components in the growth process and the incorporation of Mn acceptor states favors the formation of nitrogen vacancies. Such vacancies form shallow donor complexes and thus contribute to self-compensation, which may hamper carrier mediation. Raman spectroscopy also revealed a disorder-induced mode at 300 cm@super -1@. The intensity of both modes was found to be weaker by more than one order of magnitude compared to GaMnN grown by MBE or prepared by ion-implantation. This is a consequence of the improved MOCVD growth conditions. Crystalline integrity and the absence of major second phase contributions were confirmed by high resolution X-ray diffraction studies. Atomic force microscopy showed that optimized annealing conditions suppressed the formation of Mn-rich precipitates on the surface. Further investigations on the lattice dynamics and the determination of the optical constants were enabled by infrared reflectance spectroscopy. The GaN E1(TO) phonon frequency linearly increases with Mn composition, which is expressed by (558 + 2.7x) cm@super -1@. Meanwhile the peak values of the infrared dielectric functions of the GaMnN decrease with increasing Mn concentration.

3:00pm **MI+EM-WeA4 Epitaxial Growth of Ferromagnetic Mn@sub 3-delta@Ga Thin Films on Wurtzite GaN(0001) by Molecular Beam Epitaxy**, ***E.D. Lu****, M.B. Haider, R. Yang, C. Constantin, G. Pokharel, D.C. Ingram, A.R. Smith,* Ohio University

Magnetic metal and/or alloy films on III-V semiconductor substrates have attracted considerable interest due to the potential applications for magnetic/spintronic materials and devices,especially as spin electron injection sources for spin-sensitive heterostructures as well. The binary MnGa alloy is one of several promising metallic ferromagnetic candidates with CuAu-I type ordering. It is a face-centered tetragonal (fct) structure with lattice constants a = 3.897 Å, c = 3.58-3.65 Å dependent on content of at.% Mn between 55-60%. The epitaxial ferromagnetic Mn@sub 3-Î´@Ga(111) thin films have been grown on wurtzite GaN(0001) substrates with Ga polar surface by molecular beam epitaxy through controlling the substrate temperature and flux ratio of manganese to gallium during the growth. Prior to growing Mn@sub 3-Î´@Ga thin films, the commercial MOCVD GaN substrates were directly heated for clean up and refreshed by growth of GaN layer by radio plasma MBE. The growth and structure of the Mn@sub 3-Î´@Ga thin films are monitored in situ by reflection high energy electron diffraction (RHEED). The RHEED pattern was spotty at the initial stage and gradually became streaky, indicating surface roughness at the beginning and finally a smoother surface at the end. Combined RHEED and ex situ XRD results have revealed the primarily structure of the CuAuâ?"I type fct Mn@sub 3-Î´@Ga thin films grown with (111) plane lying on GaN(0001) plane; due to double lattice constant of the Mn@sub 3-Î´@Ga(111) plane along [11-2] direction is a good match with that distance along [11-20] direction of GaN(0001) (less than 4% mismatch), the epitaxial relationship of the fct Mn@sub 3-Î´@Ga is (111)[01-1] MnGa // (0001)[1-100]GaN and (111)[11-2] MnGa // (0001)[11-20]GaN. Rutherford Backscattering Spectroscopy (RBS) has also confirmed composition of the Mn@sub 3-Î´@Ga thin films with the ratio of Mn to Ga about 1.5 to 1.

3:20pm **MI+EM-WeA5 Nanostructure of Ferromagnetic Mn-implanted Si***,* ***C. Awo-Affouda***[1]*, M. Bolduc, K.A. Dunn, M.B. Huang, F. Ramos, G. Agnello, B.L. Thiel, V.P. LaBella,* University at Albany-SUNY

Semiconductor devices which exploit the spin of the electron hold great potential to produce devices with increased functionalities. Making conventional semiconductors ferromagnetic via ion implantation of Mn will aid in fabricating future spintronic devices. We recently demonstrated that ferromagnetism can be achieved via Mn-ion implantation of n-type and p-type Si wafers. A Curie temperature greater than 400K was observed for the p-type samples. The structure of the implanted material was investigated in order to identify the source of the ferromagnetism. SIMS depth profiling of the as-implanted samples showed a typical Gaussian shape profile of Mn atoms in the silicon lattice, which peaks at 250 nm. Post-implant annealing was performed to heal the damage from the implantation process and resulted in a strong redistribution of the Mn atoms. Furthermore diffraction contrast TEM of the annealed samples revealed nanometer size precipitates distributed throughout the implanted region, along with a large band of dislocation and stacking faults. Selected area diffraction patterns gave strong evidence that these phases are MnSi@sub1.7@ crystallites. We will discuss the role of these precipitates on the observed ferromagnetism.

3:40pm **MI+EM-WeA6 Ferromagnetic Properties of Mn-implanted Si***,* ***M. Bolduc****, C. Awo-Affouda, M.B. Huang, F. Ramos, V.P. LaBella,* University at Albany - SUNY

Integrating spintronic device concepts with silicon may enable new possibilities for fabrication. In addition, theoretical calculations have predicted ferromagnetic ordering in Mn-doped group-IV semiconductors. This potential has motivated the search for a Si-based ferromagnetic semiconductor. We demonstrate that p-doped and n-doped Si crystals can be made ferromagnetic above room temperature through Mn-ion implantation. 300-keV Mn@super+@ ions were implanted at doses of (1-10)X10@super15@ cm@super-2@ reaching peak concentrations of (0.1-0.8) at.% as measured through SIMS profiling. Ferromagnetic hysteresis loops were obtained using a SQUID magnetometer at temperature of (10-300) K, yielding a saturation magnetization of 0.1-0.7 emu/g-sample. The Curie temperature is found >400 K with carrier concentration dependence. We will report on the dependence of the magnetic properties on the post-implant annealing temperature and Mn concentration. These results will be discussed in comparison with other ion implanted or MBE grown group-IV ferromagnetic semiconductors.

4:00pm **MI+EM-WeA7 Growth and Magnetic Properties of Doped ZnO Epitaxial Films and Nanocrystal***,* ***S.A. Chambers****,* Pacific Northwest National Laboratory and Univ. of Washington*; A.C. Tuan,* Pacific Northwest National Laboratory*; K.R. Kittilstved, D.R. Gamelin,* University of Washington**INVITED**

Since 2001, researchers around the world have been involved in a vigorous search for new ferromagnetic oxide semiconductors with Curie temperatures above ambient. Such materials are vitally important for the practical realization of spintronics. Two wide bandgap oxide semiconductors have been of particular interest - TiO@sub 2@ anatase and ZnO. A number of claims of room temperature ferromagnetism (RTFM) in these host oxides with various dopants have been made. However, some of the results were based on poorly characterized material, often containing magnetic secondary phases, leading to illegitimate claims. Even for well characterized materials which are phase-pure magnetically doped oxides, the mechanism(s) of magnetism remain largely undetermined. We have used oxygen plasma assisted metal organic chemical vapor deposition along with direct wet chemical synthesis and spin coating to prepare Co@sub x@Zn@sub 1-x@O and Mn@sub x@Zn@sub 1-x@O epitaxial and nanoparticle films. Co(II) and Mn(II) substitute for Zn(II) in the wurtzite lattice in materials synthesized by both methods. Room temperature ferromagnetism in epitaxial Co:ZnO films can be reversibly activated by diffusing in Zn, which occupies interstitial sites and makes the material n-type. O-capped Co:ZnO nanoparticles, which are paramagnetic as grown, become ferromagnetic upon being spin coated in air at elevated temperature. Likewise, spin-coated N-capped Mn:ZnO nanoparticle films also exhibit room temperature ferromagnetism. However, the inverse systems, N-capped Co:ZnO and O-capped Mn:ZnO, are entirely paramagnetic when spin coated into films in the same way. Unfortunately, the nanoparticle films are not sufficiently conductive do perform magneto-transport measurements. Instead, we have carried out a detailed analysis of optical absorption, photovoltage, and magnetic circular dichroism spectra. This analysis reveals that the resonances Co(I) ↔ Co(II) + e@super

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[1] **Falicov Student Award Finalist**

-@@sub CB@ and Mn(III) ↔ Mn(II) + h@super +@@sub VB@ are energetically favorable, consistent with strong hybridization of Co (Mn) with the conduction (valence) band of ZnO. In contrast, the resonances Mn(I) ↔ Mn(II) + e@super -@@sub CB@ and Co(III) ↔ Co(II) + h@super +@@sub CB@ are not energetically favorable. These results indicate that Co(II)-derived states will strongly interact only with the conduction band, whereas Mn(II)-derived states interact strongly only with the valence band. These spectral results are consistent with the observed ferromagnetism in Co:ZnO (Mn:ZnO) being mediated by electrons (holes). @footnoteText@This work was performed in part in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory. This work was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Materials Science and Engineering Physics. Work at UW was funded by the NSF (DMR-0239325 and ECS-0224138) and the Research Corporation.

4:40pm **MI+EM-WeA9 Effects of Differing Mn@sub Ga@/Mn@sub I@ on the Anomalous Hall Effect in (Ga,Mn)As**, *Y.S. Kim, H.K. Choi, Z.G. Khim,* Seoul National University, Korea*; S.H. Chun,* Sejong University, Korea*; **Y.D. Park**,* Seoul National University, Korea

We report on the effect of differing ratios of substitutional and interstitial Manganese (Mn@sub Ga@/Mn@sub I@) on the Anomalous Hall Effect(AHE) in low temperature molecular beam epitaxy prepared (Ga,Mn)As diluted magnetic semiconductors. As-grown (Ga,Mn)As epifilms with Mn content from 2.4 % ~ 6.1 % exhibit ferromagnetic ordering below temperatures ranging from 60 to 110 K. Relatively differing Mn@sub Ga@/Mn@sub I@ ratios were achieved by careful annealing at moderate temperatures as evident in the differing resistivities (as low as 2.5 m@ohm@-cm)/ Hall carrier concentrations (as high as ~ 8 x 10@super 20@cm@super -3@) as well as T@sub C@ (as high as 150 K) with optimal annealing temperature found to be 250°C.@footnote 1@ AC-magnetotransport measurements conducted from 5 K to 300 K and with applied magnetic fields ranging to +/- 7 Tesla indicate similar field dependence of resistivity, AHE, and metal-insulator-like transition near T@sub C@ as reported by others.@footnote 2@ T@sub C@'s as found from Arrott plots from the resulting AHE measurements agree well with direct SQUID magnetometry measurements. Log-log plots of @rho@@sub xy@, d@rho@@sub xy@ /dH, and @rho@@sub xy@/M@sub S@ vs. @rho@@sub xx@, cumulated from AHE measurements at temperatures below T@sub C@ of differing as-grown Mn content and annealing conditions, indicate skew scattering to be the dominant mechanisms for AHE in (Ga,Mn)As regardless of as-grown Mn content or Mn@sub Ga@/Mn@sub I@ ratios and possibly regardless of presence of non-magnetic or magnetic Mn-rich nano-clusters. We will also discuss the results in light of theory@footnote 3@ of AHE in clean (Ga,Mn)As and experimental reports@footnote 4@ of AHE in DMS systems with ferromagnetic nano-clusters. @FootnoteText@ @footnote 1@T Hayashi et al. APL 78, 1691 (2001); KC Ku et al., APL 82, 2302 (2003).@footnote 2@M Tanaka, JVST B 16, 2267 (1998).@footnote 3@T Jungwirth et al., PRL 88, 207208 (2002).@footnote 4@SR Shinde et al., PRL 92, 166601 (2004).

Manufacturing Science and Technology
Room 207 - Session MS-WeA

Metrology & Process Control for Advanced Manufacturing

Moderator: S. Shankar, Intel Corporation

2:00pm **MS-WeA1 Optical Interferometric Microscope for Real-Time Monitoring and Control of Focused Ion Beam Processes**, *D.P. Adams, M.B. Sinclair, T.M. Mayer, **M.J. Vasile**, W.C. Sweatt,* Sandia National Laboratories

Focused ion beam (FIB) techniques have a wide range of applications including lithographic mask repair, specimen preparation, semiconductor analysis and nanodevice prototyping. Although FIB systems offer excellent in-plane spatial resolution, these do not include instrumentation that actively monitors milled feature depth. In order to enhance the control of FIB systems, we have designed, fabricated and tested a custom optical interferometer microscope suitable for operation during processing. This Michelson interferometer is intended for real-time monitoring and feedback control of focused ion beam processes including sputtering. The apparatus is designed for minimal outgassing / UHV operation, and the optics are retractable (within the vacuum system) providing ample space when removed for other commonly-used diagnostic tools and gasjet assemblies. The optical path and ion beam vector are co-incident at the sample. This is made possible through use of a pinhole mirror that is positioned between the exit aperture of the ion gun and the specimen. Long working distance (39 mm), high numerical aperture (NA = 0.39) objectives have been custom designed and fabricated for the interferometer. Tests with FIB-milled Si samples demonstrate 1.0 micron optical in-plane resolution. Out-of-plane resolution is approximately 1-2 nm.

2:20pm **MS-WeA2 Method for Creating Cross-Sectional TEM Single Crystal Diamond Samples using Focused Ion Beam and In-Situ Lift Out**, ***D.P. Hickey**, E. Kuryliw, K.S. Jones,* University of Florida

A method is described for creating a transmission electron microscope (TEM) cross section of single crystal diamond using a focused ion beam (FIB) and in-situ lift-out. The method results in samples less than 50 nm thick at the tip and approximately 100-300 nm thick across the length, and does not require a large amount of starting material. Few TEM studies of single crystal diamond have been reported, most likely due to the time and difficulty involved in sample preparation. This technique can create a cross-sectional TEM sample in less than five hours. Creating cross-sectional TEM samples for single crystal diamond are slightly different than silicon due to the exceptional hardness and insulating properties of the diamond. The method also allows for additional thinning for use with high-resolution TEM imaging. The method is applied to oddly shaped diamond samples, and does not require a wafer-flat sample to create a TEM sample. This sample preparation technique has been applied to the study of ion implantation damage in single crystal diamond and its evolution upon annealing.

2:40pm **MS-WeA3 Temperature and Film Thickness Sensor for Substrates with Multi-layered Thin Films using Optical Fiber type Low-coherence Interferometry**, ***T. Ohta**,* Wakayama University, Japan*; K. Takeda,* Nagoya University, Japan*; M. Ito,* Wakayama University, Japan*; C. Koshimizu,* Tokyo Electron AT LTD., Japan

The temperature control of substrates is very significant to fabricate much finer and deeper patterns in ultra-fine processing technologies such as plasma processes. So we have developed a temperature sensor for measuring the temperature of each layer of multi-layered substrates, such as Silicon On Insulator (SOI), using a low-coherence interferometer and a Michelson interferometer. This system consisted of Super Luminescent Diodes (SLD:1550nm and 1310nm), a Laser Diode (LD:850nm), a scanning mirror, optical fibers, etc. We measured the temperature of multi-layered substrates of Si/SiO@sub 2@/Si=300µm/500µm/300µm, and as a result, we have found that this system has the resolution of 1 °C. However, this system had difficulty in measuring the temperatures of substrates with thin film layers, which have the optical pass length less than the coherent length of a low-coherent light source. To solve this problem, we have proposed a novel measurement for measuring the thickness of the thin film layer as well as the temperature of substrates. The thickness of the thin film was measured from the ratio of interference intensity of SLDs and the measured value corresponded with theoretical value within 2 micron of thickness. By estimating the film thickness the effect of interference overlapping was reduced, thus improving the error rate of temperature measurement.

3:00pm **MS-WeA4 Endpointing Chamber Clean by Calorimetric Probing of Plasma Effluent**, ***I.S. Chen**, J.W. Neuner, J.J. Welch, P.S.H. Chen, F. DiMeo,* ATMI

The semiconductor industry employs gas-phase cleaning widely to remove materials deposited on the chamber walls during thin film deposition processes. Chamber clean endpointing - i.e., terminating the process when the chamber is clean - is desirable to manage cost-of-ownership and environmental impact. Existing endpointing methods tend to rely on changes of plasma characteristics as the in situ plasma removes the deposit in time. Chamber clean technology is moving towards remote generation of plasma species for cleaning. In this arrangement, the chamber is located downstream from the plasma source. Because the etching reaction occurs ex situ, there are no relevant changes occurring in the plasma characteristics, and the effectiveness of many existing methods decreases. We report the development of a calorimetric probe for chamber clean endpointing. The probe has an all solid-state construction and is engineered to immerse in the plasma effluent during endpointing operation. The probe measures the heat flux carried by the effluent, and the signal has been shown to correlate with chamber condition. By virtue of its downstream location, the probe operation does not depend on the plasma sourcing scheme (in situ vs. remote). We demonstrate successful endpointing for in situ chamber clean of TEOS deposition process on a

PECVD tool. The probe results compare favorably with other co-installed endpointing solutions.

3:20pm **MS-WeA5 Sensing and Control Strategies for Spatially Programmable CVD**, ***Y. Cai,*** *R. Sreenivasan, R. Adomaitis, G.W. Rubloff,* University of Maryland

A multiplexed mass spectrometric gas sampling system was designed and implemented for real-time, in situ measurement of gas species concentrations in a spatially programmable chemical vapor deposition (SP-CVD) reactor, a new paradigm for equipment design based on a segmented gas injection showerhead with exhaust gas recirculation up through the showerhead (U.S. Patent No. 6,821,910). To extend chemical sensing and metrology techniques developed for conventional CVD reactors to this new reactor configuration, we have developed a multiplexed gas sampling system based on a dynamic simulation of the sampling system, and demonstrated it in the SP-CVD reactor. Built on a three-segment SP-CVD prototype reactor, the gas sampling system was used to assess experimentally reactant gas transport mechanisms, focusing on: (1) inter-segment gas diffusion through the gap between showerhead and wafer surface; and (2) gas back diffusion through the common exhaust volume above the showerhead. We quantified the contribution of each transport mechanism to gas phase composition measured in each segment by fixing the sampling tube position and varying the gap dimension between the wafer and the movable showerhead. W CVD experiments using H2 reduction of WF6 were used to establish a model describing the relationship between the time integrated HF reaction product signal from the mass spectrometer and post-process thickness measurements obtained from four-point-probe maps of sheet resistance. Thickness metrology with precision of 3-4% has been obtained, approaching the desired range of thickness control precision. We expect that this sensing methodology not only will enable real-time spatially-distributed end point control, but also will make it possible to guide rapid reprogramming of process recipes intended to achieve simultaneously high material quality and uniformity, or to serve as a valuable asset to potential combinatorial experimental capabilities of the SP-CVD reactor.

3:40pm **MS-WeA6 High Resolution 2D dopant profiling of FinFET Structures and Silicon-based Devices using Scanning Probe Microscopies**, ***A.A. Khajetoorians,*** University of Texas at Austin; *X.-D. Wang,* Freescale Semiconductor Inc.; *J. Li,* University of Texas at Austin; *D. Pham,* International Sematech; *A.C. Diebold,* International Sematech, US; *C.K. Shih,* University of Texas at Austin

The ability to perform dopant/junction profiling with high spatial resolution is critical for development of future generation devices such as FinFET structures. Among various forms of scanning probe microscopy, scanning tunneling microscopy (STM) has demonstrated direct atomic imaging of dopant atoms on GaAs (110) surfaces. More recently, scanning thermoelectric microscopy (SThEM) (H.K. Lyeo et al Science v.303 p816 (2004)) has been applied to profile GaAs p-n junction with unprecedented spatial resolution. The key challenge to successfully apply these techniques to silicon-based devices is to prepare a surface that is both chemically and electronically passivated. Here we present our progress toward this goal. We present STM and SThEM studies on Si p-n junction devices including FinFET structures. We also present in-depth profiling of fin structures using scanning capacitance (SCM) and conductive atomic force microscopy (C-AFM).

Nanometer-Scale Science and Technology
Room 210 - Session NS-WeA

Nanopatterning and Manipulation

Moderator: S.W. Pang, University of Michigan

2:00pm **NS-WeA1 Molecular Ruler Lithography Process with Sacrificial Multilayer Host Structures Incorporating a Barrier Layer**, ***S. Subramanian,*** *J.M. Catchmark,* Pennsylvania State University

Molecular ruler lithography has the potential of improving the achievable resolution of conventional lithography techniques, without resorting to new instrumentation. This is accomplished by scaling down the dimensions of functional host structure by selectively assembling organic molecules of precise length on their surface.@footnote1@ A novel method for performing molecular ruler lithography using sacrificial host structures has recently been developed and demonstrated using contact lithography.@footnote2@ This new approach provides a reproducible,high yield technique for selective removal of the host,fabricating high aspect ratio structures and isolation of the host material from the substrate. In order to make this process widely compatible with optical and electron beam lithography techniques, we introduce a modified molecular ruler lithography process using a sacrificial multilayer host structure which incorporates a barrier layer in between the sacrificial and the host material. This barrier layer prevents the lithography resist,developer and removal chemistries used to pattern the host material from interacting with the sacrificial material. We demonstrate this process by using contact lithographically patterned gold host structures to produce isolated platinum lines. The process consisted of depositing a sacrificial LOR resist (MicroChem) and a chrome barrier layer. A gold host feature was patterned on top of the chrome barrier layer using optical lithography. The chrome barrier was then selectively removed using reactive ion etching. Mercaptohexadeconoic acid molecules were assembled onto the patterned gold layer completing the fabrication of the sacrificial host structure. Platinum was then deposited and the host structure was selectively removed by dissolving the sacrificial LOR layer to leave behind the isolated platinum lines. @FootnoteText@ @footnote 1@Hatzor A, Weiss P, Science 291,1019. @footnote 2@Subramanian S, Catchmark J, JM3, accepted, 2005.

2:20pm **NS-WeA2 High Electric Field Nanoimprint Lithography of Metal Thin Films**, ***N. Farkas,*** *P. Meduri, E.A. Evans, R.D. Ramsier,* The University of Akron; *J.A. Dagata,* National Institute of Standards and Technology

Sputter-deposited ZrN thin films prepared with high nitrogen content exhibit superdiffusive scanning probe microscope (SPM) oxidation kinetics and oxide feature heights of several hundred nanometers. We extend this enhanced single-tip SPM oxidation to parallel writing with an inherently simple method to obtain large areas of submicrometer-scale oxide features on ZrN thin films. To investigate if this nanoimprint lithography technique can be used to create arrays of well-defined features on other metal surfaces, pattern transfer onto iron/iron nitride thin films is studied here. This comparison is of fundamental interest in that Zr oxidation is driven by oxygen migration, whereas Fe oxidizes by metal ion transport. Implication of the use of patterned Zr and Fe nitride thin films for biomedical and magnetic applications are also discussed.

2:40pm **NS-WeA3 Thermolithography for Micro- and Nanofabrication**, ***M.-T. Hung,*** *Y.S. Ju,* UCLA

An intriguing class of alternative lithography techniques utilize localized heating to create nanoscale features.@footnote 1@ The so-called thermolithography is very interesting since heat conduction in highly disordered polymer layers is a relatively slow diffusive phenomenon, which can be exploited to fabricate 3D nanostructures. We present our study of one type of thermolithography techniques that induces thermochemical cross-linking in select areas of a thin polymer layer. The patterned polymer layer can serve as part of a device or as a mask for subsequent processing. We demonstrate fabrication of T-gate structures and negative-slope resist profiles advantageous for the lift-off process. The thermal transport properties of polymer layers and kinetics of cross-linking processes are key parameters that determine the speed and resolution limit of the thermolithography techniques. We develop thermal transport property measurement techniques based on microfabricated ultra-thin membrane structures. The thermal conductivity and heat capacity of commercially available image reversal photoresists are determined before and after UV exposure, before and after postexposure bake, and also as a function of temperature. We also use micro-fabricated heaters coated with a polymer layer to induce precisely controlled heating and study kinetics of cross-linking. The spatial extent of cross-linking is determined by treating the polymer in a developer and examining the profile of the remaining layer using an SEM. The polymer profiles are compared with numerical heat conduction simulation results to extract the threshold cross-linking temperature as a function of heating duration. The present work demonstrates feasibility of a thermolithography technique and provides important data on the thermal transport properties and kinetics of polymerization that help guide further development of micro- and nano-scale thermolithography techniques. @FootnoteText@ @footnote 1@ A. S. Basu, S. McNamara, and Y.B. Gianchandani,J.Vacuum Sci. & Tech. B, 2004, 22, pp. 3217-3220. M. Kuwahara , J.H. Kim , J. Tominaga, Microelectronic Engineering, 2003, 67-68, pp. 651-656

3:00pm **NS-WeA4 Direct Deposition of Molecular Electronics Materials using Thermal DPN***, **P.E. Sheehan**, M. Yang, A.R. Laracuente,* Naval Research Laboratory*; B.A. Nelson, W.P. King,* Georgia Tech*; L.J. Whitman,* Naval Research Laboratory

We have developed a new technique, called thermal DPN (tDPN),@footnote 1@ where a heated atomic force microscope cantilever controls the deposition of a solid "ink." The heated cantilever can be used like a nanoscale "soldering iron" or "glue gun" to deposit semiconductors, insulators, or metals. tDPN has several advantages over conventional DPN. Control over writing is much greater--deposition may be turned on or off and the deposition rate changed without breaking contact with the surface. In addition, imaging with a cool tip does not appear to contaminate the surface, thereby allowing in situ confirmation of the deposited pattern. tDPN also expands the range of useable inks to those that are immobile at room temperature. Finally, multi-layer films can be deposited sequentially, enabling 3-D structures and heterostructures to be written directly. One material that is easily deposited by tDPN but which is challenging by other means is poly(3-dodecylthiophene), or PDDT. PDDT is a conducting polymer that shows great promise as an active component in organic electronic devices. Using tDPN, well-ordered PDDT nanostructures have been deposited on silicon oxide and gold surfaces with layer-by-layer thickness control. By adjusting the tip heating power and the writing speed, we can vary the polymer thickness from a single monolayer (~2.6 nm) to tens of monolayers with lateral dimensions below 100 nm. Unlike conventional DPN inks, this low vapor pressure polymer may be deposited in UHV by tDPN, thereby allowing integration with CMOS processing. Along with our success at depositing metallic indium nanowires via tDPN, we now have all the requisite elements for the direct deposition of electronic circuitry. @FootnoteText@ @footnote 1@ P. E. Sheehan, L. J. Whitman, W. P. King, B. A. Nelson, Appl. Phys. Lett. 85, 1589 (2004).

3:20pm **NS-WeA5 Physical Processes in Atom Manipulation and Creation of Novel Nanostructures of Co and Cu Atoms on Cu(111) Surfaces****, **J.A. Stroscio**, R.J. Celotta,* NIST **INVITED**

We are studying the interactions involved in STM atom manipulation using Co and Cu atoms on a Cu(111) surface@footnote 1@ and building novel CoCu nanostructures using atom manipulation. The interactions responsible for atom manipulation are investigated by measuring the atom dynamics with a STM using both imaging and tunneling spectroscopy methods. Manipulated atom imaging, where the manipulated atom is rastered in the trapping potential of the STM tip, reveals the binding sites of the substrate. Contrast in this new type of image is due to the tip sensing the presence of the adatom, which can reflect atom motion and a variation in the local potential energy surface. Quantitative measurements of atom dynamics are made by studying the tunneling current noise properties during atom manipulation. Two distinct mechanisms of atom motion can be identified in the noise dynamics; quantum tunneling of the adatom between neighboring lattice sites, and vibrational heating of the adatom by inelastic electron scattering. The magnetic Co atom is a Kondo impurity on Cu(111) surfaces at low temperatures. The interaction between Co and Cu can be tuned by varying the Cu coordination in nanostructures built by atom manipulation. These nanostructures show significant changes in the Kondo density of states resonance as a function of Cu coordination. *This work is supported in part by the Office of Naval Research. @FootnoteText@@footnote 1@J. A. Stroscio and R. J. Celotta, Science 306, 242 (2004).

4:00pm **NS-WeA7 Chemically Engineering the Motion of Individual Molecules on the Si(100)-2x1 Surface: a Scanning Tunneling Microscopy Study***, **R. Basu**, J.D. Tovar, M.C. Hersam,* Northwestern University

Room temperature ultra-high vacuum (UHV) scanning tunneling microscopy (STM) is used to study a unique bond-breaking mediated motion of individual organic molecules on the clean Si(100)-2x1 surface. Specifically 4-methoxystyrene molecules are observed to undergo switching between two cycloaddition conformations mediated by pivotal motion about one Si-C bond. Styrene molecules, on the other hand, do not undergo such lateral translations, thus suggesting that the rotational degree of freedom of the methoxy group is responsible for the apparent motion of 4-methoxystyrene. To test this hypothesis, the rotational degree of freedom of the methoxy group was suppressed by synthesizing an analog molecule (5-vinyl-2,3-dihydrobenzofuran) where the methoxy group is covalently linked back to the aromatic ring. UHV STM imaging of 5-vinyl-2,3-dihydrobenzofuran on clean Si(100)-2x1 indeed confirms the suppression of molecular motion. This study suggests that the motion of organosilicon adsorbates can be controlled by chemically engineering their intramolecular degrees of freedom.

4:20pm **NS-WeA8 Formation of Large-Area Nanostructures on Si and Ge Surfaces during Low-Energy Ion Beam Erosion***, **B. Ziberi**, F. Frost, B. Rauschenbach,* Leibniz-Institut für Oberflächenmodifizierung e.V. Leipzig, Germany

In contrast to advanced lithographic methods and subsequent etching procedures for pattern production with structure size < 100 nm, which are complex technological processes, self-organized spontaneous pattern formation during low-energy ion beam erosion is a cost-efficient `bottom up` approach for the fabrication of large-area nanostructures. The formation of these patterns can be observed on various semiconductor materials and is attributed to a surface instability between curvature dependent sputtering that roughens the surface and smoothing by different surface relaxation mechanisms. In these work results for pattern formation due to low-energy noble gas (Ne@super +@, Ar@super +@, Kr@super +@, Xe@super +@) ion beam erosion of silicon and germanium surfaces at oblique ion incidence with and without sample rotation are presented. Depending on ion beam parameters, i. e. ion energy, ion incidence angle and ion mass, different patterns can evolve on the surface. In the case with sample rotation, very well ordered dot structures evolve on the Si surface at glancing incidence angle of 75° with respect to surface normal, with size varying from 30 nm to 50 nm. Without sample rotation, at small ion incidence angles, remarkably high ordered ripple patterns with wavelength ~ 50 nm can form on both materials for similar sputtering conditions. By further increasing the ion incidence angle a transition from ripples to highly hexagonally ordered dot structures with periodicity of ~ 40 nm are observed. The lateral ordering of nanostructures increases with erosion time, leading to very well ordered and homogenous structures. The mean size of nanostructures can be adjusted with ion energy while maintaining their lateral ordering. Scanning force microscopy (AFM) and high-resolution transmission electron microscopy (HRTEM) were used to study the lateral ordering, shape, and size of these nanostructures.

4:40pm **NS-WeA9 Thermally Assisted Atom Transfer on Surfaces: Between Tunneling and Activated Diffusion***, **J.W. Gadzuk**,* NIST

The low temperature rates for site-to-site transfer of single atoms and molecules adsorbed on surfaces have been determined in recent STM studies@footnote 1@ within the temperature regime where the dominant transfer mechanism changes from mostly activated transmission over to thermally assisted tunneling through the inter-site (transition state) barrier, as the temperature is reduced. A model that has provided useful conceptual and quantitative insights into thermally assisted field emission tunneling spectroscopy@footnote 2@ is used here as the basis for theory of site-to-site atom transfer in this temperature range where proper account of tunneling and quantum reflection, for energies below and above the transition state barrier is required. The predicted transfer rates which are very sensitive to barrier shape as well as height, agree well with those observed in the STM studies of Co and Cu on Cu(111) surfaces in the interesting 4K@<=@T@<=@7K transition range which is relevant in the atom-by-atom fabrication of thermally stable surface nanostructures. @FootnoteText@ @footnote 1@J. Repp, G. Meyer, K.-H. Rieder, and P. Hyldgaard, Phys. Rev. Letters, Vol.91, 206102 (2003); J. A. Stroscio and R. J. Celotta, Science, Vol.306, 242 (2004).@footnote 2@J. W. Gadzuk and E. W. Plummer, Phys.Rev.B Vol.3, 2125 (1971).

5:00pm **NS-WeA10 Patterning of Well-Ordered PZT Nanodot Arrays using Silicon Nitride Shadow Mask***, **H.-J. Shin**, J.H. Choi, H. Yang, Y.D. Park, Y. Kuk,* Seoul National University, Korea*; C.J. Kang,* Myungji University, Korea

We patterned well ordered arrays of Pb(Zr@sub 0.2@Ti@sub 0.8@)O@sub 3@ nanodots on a SrRuO@sub 3@/SrTiO@sub 3@ substrate by pulsed laser deposition. A silicon nitride shadow mask with ordered holes was used for patterning of PZT arrays. This method have an advantage that deposition could be done at high temperature, which could be applicable to in situ deposition avoiding any possible contamination in dot formation. In addition, we could change the shape or size of the patterns if necessary. The SrRuO@sub 3@ bottom electrode and PZT nanodots were deposited at 760 @super o@C and 660 @super o@C, respectively. The lateral size of the dot was about 120 nm and the height was about 15 ~ 20 nm. The inter-dot distance of PZT dot arrays was about 200 nm, exactly the same as the pore-to-pore distance of the shadow mask. Each dot was fully arranged and well isolated, having dome shape after deposition. The local switching of a single dot was examined using piezoresponce force microcopy. We could observe that the absolute piezoresponse value of positively polarized dot is 28.3 % larger than that of negatively polarized background, and there weren't any noticeable inhomogeneity such as an inversion of center region after polarization. The polarized states were maintained at 61.3 % of initial value after ~ 20 min, which almost relaxed suddenly to noise level after 30 min. A sudden drop of polarization implies that the relaxation is mainly related to the nucleation stages of domain reversal in our case.

Plasma Science and Technology
Room 302 - Session PS-WeA

Atmospheric Plasmas and Microdischarges

Moderator: L. Bardos, Uppsala University, Sweden

2:00pm **PS-WeA1 Limitations for Replacement of Low Pressure Plasma by Atmospheric Pressure Plasma***, **D. Korzec,*** German University in Cairo - GUC, Egypt **INVITED**

A substantial research effort in recent years was focussed on the development of atmospheric pressure plasma (APP) for technological applications. For some applications such as surface treatment or rapid film removal the technological progress is fast and processes are available, being an alternative for the well established low pressure plasma approaches. For other applications, such as high quality film deposition or anisotropic structuring, the application of APP faces serious difficulties. These problems are discussed from the point of view of fundamental physical limitations. The different type of pressure scaling rules are critically reviewed, leading to the conclusion that APP works not because of scaling, but because of specific physical phenomena, which are significant in the pressure range over 100 Torr but can be disregarded for lower pressures. Special focus will be on the dynamics of the APP discharges and effective life times of species used for driving the APP processes. In this context, the frequency ranges for APP generation are investigated. It is shown, that only very narrow parameter windows and only selected gas mixtures allow the successful processing. Different types of APP discharges will be analyzed from the point of view of the basic physical limitations. Conclusion from this analysis will be the estimation of future trends in technological applications of APP and the definition of realistic process challenges.

2:40pm **PS-WeA3 Cold Atmospheric Plasma in Nitrogen and Air Generated by the Hybrid Plasma Source***, **H. Barankova**, L. Bardos, D. Söderström,* Uppsala University, Sweden

Generation of long plumes of cold atmospheric plasma in nitrogen and air has been successfully performed by the Hybrid Hollow Electrode Activated Discharge (H-HEAD) source. The source with a simple cylindrical electrode terminated by a gas nozzle combines the microwave antenna plasma with the hollow cathode plasma generated inside the gas nozzle by pulsed DC power. The H-HEAD source is capable to generate up to 10 cm long plumes in air at the microwave power below 500 W and at air flow rate as low as 100 sccm. Corresponding flow rates in nitrogen plasma are even less than 80 sccm. The discharges in air and nitrogen have similar shapes and are comparable with corresponding plasma columns in argon. Comparison of optical emission spectra of the plasma in nitrogen and air are presented. Temperatures generated on steel substrates by interaction with nitrogen and air plasma columns at different microwave and DC powers are compared with corresponding effects in argon plasma.

3:00pm **PS-WeA4 Ultra Fast Surface Modification Processes Employing Compact Non-Equilibrium Atmospheric Pressure Plasmas***, **N. Yoshida**,* Fuji, Machine Mfg. Co., Ltd., Japan*; H. Kano,* NU-EcoEngineering, Japan*; S. Den,* Katagiri Engineering Co., Ltd, Japan*; M. Hori,* Nagoya Univ., Japan

In the atmospheric pressure plasma processing, the vacuum facilities are basically not needed and the plasma chemistry with considerably large amount of radicals can be utilized. Consequently, the high-speed material processes such as etching, deposition and surface treatment will be potentially realized employing atmospheric pressure plasmas and the equipment cost can be drastically reduced compared with other plasmas. Up to now, many generation technologies of atmospheric pressure plasma have been proposed. We have developed the compact non-equilibrium atmospheric pressure plasma employing new type of micro-hollow cathodes. This device was constituted of the electrode with double micro-hollow structures, which is a very compact size of several ten micrometers and very light weight. Furthermore, it enables to generate the stable plasma in the atmospheric pressure condition. In this study, this plasma was generated with supplying voltage to two special hollow cathode electrodes, and throwing the argon gas of 500ml per minute into the both electrodes. The atmospheric pressure plasma generation can be realized not only in argon but also in air. When this plasma was irradiated on the glass surface for a short time, the considerable change was observed on the surface of the glass. XPS analysis indicated that the C-O bond on the glass surface was drastically decreased while a new peak of O=C-O bond appeared during the plasma irradiation. After only 0.08 seconds irradiation, the contact angle of 20 degree was obtained and after 0.4 seconds, that of 8 degree was easily realized. Therefore, the high hydrophilic processing was successfully achieved in a very short time by using this plasma. From these results, the compact non-equilibrium atmospheric pressure plasma developed in this study will be very promising for a lot of applications to various kinds of surface treatment fields.

3:20pm **PS-WeA5 Design, Diagnostics, and Applications of Microplasmas Operated at around Atmospheric Pressure***, **K. Tachibana**,* Kyoto University, Japan **INVITED**

Recently, microplasmas of sub-millimeter to micrometer scales are of much interest for various applications such as displays, light sources, micro total analytic systems, micromachining tools, and so on. Microplasmas can be operated not only as a sole device but also in one or two dimensional arrays. In addition, those are operated at a higher pressure range, including atmospheric pressure, according to the shrinkage of the sizes. These features make their potential larger for wider applications. If we use gas discharges for the generation of microplasmas, the electrode configuration is categorized as counter, coplanar, and coaxial electrode types. The dielectric barrier discharge (DBD) scheme is also advantageous in their parallel operation in arrays, where electrodes are covered by dielectric materials for preventing the current concentration automatically thanks to the accumulated surface charge. As the first example, several types of microdischarges are introduced which are used in plasma display panels. Experimental results on spatiotemporal behaviors of microplasmas in unit discharge cell are explained, where the excited species have been diagnosed by using a laser absorption spectroscopy method and the electron density by a mm-wave transmission technique. Those results are discussed for the improvement of luminous efficiency. As the second example, a coaxial mesh-type DBD with a microplasma integrated structure is explained as a large area plasma source for the purpose of various surface treatment technologies. The superior performances are explained in a comparison with those of a conventional parallel plate DBD system for the wider parameter ranges of stable operations. As the third example, our new idea of microplasma devices for the control (switching, filtering, etc.) of microwaves will be explained by using the dielectric properties of plasmas. This idea can be expanded towards microplasma photonic crystals.

4:00pm **PS-WeA7 A Non-Equilibrium Atmospheric Pressure Plasma Operating at High Power Densities***, **M. Moravej**,* University of California, Los Angeles*; X. Yang,* Researcher*; J. Penelon, S. Babayan,* Surfx Technologies*; R.F. Hicks,* University of California, Los Angeles

A new atmospheric pressure plasma source has been developed that shows exceedingly high processing rates. For example, kapton films have been etched at 5.0 mm/s using an argon and oxygen discharge with 6.0 vol.% O2 and a temperature of 280 Â°C. The plasma source consisted of a small quartz tube that was capacitively coupled to radio frequency power at 13.56 MHz. The input plasma power could be increased up to 150 W/cm3 without arcing, or forming a streamer like discharge. At this power density, the gas temperature was determined by spectroscopic methods to be 300Â±30 Â°C. The O atom concentration was measured in the plasma afterglow by nitric oxide titration, and was found to be 1.2Â±0.6 Â´1017 cm-3 at 150 W/cm3 and 6.0 vol.% O2 in Ar. This corresponds to 15% dissociation of the oxygen molecules fed to the source. The concentration of ozone in the downstream region equaled 4.3Â±0.5 Â´1014 cm-3, as determined by UV absorption spectroscopy. These results were found to be in good agreement with a numerical model of the plasma and afterglow that included the reaction mechanism and the plasma electron density and temperature as calculated from current-voltage measurements. At the meeting, we will discuss the physics and chemistry of this new atmospheric plasma in detail. We will also present results on materials processing with this device, such as silicon dioxide etching and/or thin film deposition.

4:20pm **PS-WeA8 Modeling of Pulsed Microdischarges for use as Thrusters@footnote 1@***, **R.A. Arakoni**,* University of Illinois at Urbana-Champaign*; J.J. Ewing,* Ewing Technology Associates*; M.J. Kushner,* Iowa State University

Microdischarges having characteristic dimensions of 100s of µm with back pressures of 10s to 100s of Torr are being investigated for use as sources of thrust for small satellites. These devices are capable of generating up to mN of thrust using noncontaminating propellants such as rare gases. The class of device of interest is a cylindrical discharge operated in dc or pulsed modes. The bore of the discharge is fabricated in a heat-resistant ceramic with micro-fabricated ring electrodes. The dominant mode of propulsion is thermal heating of the neutral gas by the discharge, primarily by charge exchange. In this talk, this class of microdischarge will be computationally investigated using a 2-dimensional plasma hydrodynamics model having an unstructured mesh to resolve non-equilibrium electron, ion and neutral transport using fluid equations.@footnote 2@ Sheath accelerated, beam-like electrons are resolved using a Monte Carlo simulation. A compressible Navier-Stokes module provides the bulk fluid velocities and temperatures. Changes in surface properties are addressed with a surface site-balance model. Results from a parametric investigation of back pressure (a few 10s to 100s of Torr), power, and pulse length will be discussed for rare gas mixtures with the goal of maximizing the velocity of the exhaust at the exit plane. Velocities of up to 100s m/s have been predicted in the throats of the devices with plasma densities of 10@super 13@ - 10@super 14@ cm@super -3@ with back pressures of 50 Torr in a cw operation mode. Since the source of propulsion is plasma heated gas, the siting of the plasma within the bore of the microdischarge, and subsequent heat transfer to the walls, is an important design consideration. @FootnoteText@ @footnote 1@ Work supported by Ewing Technology Associates, NSF (CTS03-15353) and AFOSR. @footnote 2@ A. N. Bhoj and M. J. Kushner, J. Phys. D, 37, 2910 (2004).

4:40pm **PS-WeA9 Atmospheric Microplasma-on-a-Chip Operating in Air***, **J. Hopwood**,* Northeastern University*; F. Iza,* Pohang University of Science & Technology, Korea

In this paper, an atmospheric pressure plasma-on-a-chip operating in air is described. The microplasma is ignited and sustained by microwave power (900 MHz, 3 watts) from a common cell phone power amplifier. The discharge is sustained within a 25µm gap formed in a microstripline split-ring resonator. The microstrip transmission lines are surface micromachined on a 22 mm diameter aluminum oxide wafer using electroplated copper and gold. The high quality factor (Q) and narrow discharge gap of the split-ring resonator result in electric field strengths in excess of 10 MV/m prior to plasma ignition. The discharge appears as an intense filament, but is not in thermal equilibrium as the measured rotational temperatures for the second positive system of nitrogen are 500-700 K in atmospheric pressure air. The impedance of the microplasma is found by measuring the microwave reflection coefficient of the resonator as a function of frequency. From the plasma impedance, the electron density is found to be on the order of 10@super 14@ cm@super -3@ in atmospheric pressure argon. Lifetime testing shows that the micro-electrodes are not eroded by ion bombardment after 100 hours operating in air at 3 watts. Applications for this microplasma include portable chemical analysis by optical emission spectrometry and ion mobility spectrometry. This work is supported by the NSF under Grant No. DMI-0078406.

5:00pm **PS-WeA10 Diagnostics and Simulations of a Helium Micro-Discharge at Atmospheric Pressure***, **Q. Wang**, D.J. Economou, V.M. Donnelly,* University of Houston*; I. Koleva,* University of Sofia

Spatially resolved measurements (resolution ~ 6 µm) were taken across an L=200 µm slot-type discharge in an atmospheric pressure direct current helium microplasma. Gas temperature profiles were determined from N@sub 2@ emission rotational spectroscopy. Stark splitting of the hydrogen Balmer-@beta@ line was used to investigate the electric field distribution in the cathode sheath region. Electron densities were evaluated from the analysis of the spectral line broadenings of H-@beta@ emission. The gas temperature was between 350 and 550 K, peaking nearer the cathode and increasing with power. The electron density in the bulk plasma was in the range 4-7 x 10@super 13@ cm@super-3@. The electric field peaked at the cathode (~60 kV cm@super -1@) and decayed to small values over a distance of ~ 50 µm (sheath edge) from the cathode. These experimental data are in generally good agreement with a self-consistent one-dimensional model of the discharge. The influence of gas heating on the discharge properties (such as current-voltage characteristic, cathode and anode sheath profiles), was also investigated. As the discharge current increased, the simulations indicate that the anode sheath turned from a positive ion sheath to an electron sheath, with concomitant changes in the sheath electric field profile and direction. This can be explained, based on the balance of charged particle gain and loss. Gas flow does not have a significant effect on gas temperature because of the high thermal conductivity of helium.

Surface Science
Room 202 - Session SS+EM-WeA

Organic Film Growth and Characterization

Moderator: J.N. Russell, Jr., Naval Research Laboratory

2:00pm **SS+EM-WeA1 Comparison of the Electronic Structure of Ferroelectric Polymers***, **J. Xiao**, L.G. Rosa, M. Poulsen, D.Q. Feng, S. Ducharme,* University of Nebraska-Lincoln*; P.A. Dowben,* University of Nebraska-Lincoln, US

We compare the electronic structure of copolymers of polyvinylidene fluoride with trifluroethylene P(VDF-TrFE, 70%:30%) with polymethylvinylidenecyanide (PMVC). Crystalline thin films can be formed from both ferroelectric polymers and we find that in both cases the dipole is aligned along the surface normal. The P(VDF-TrFE) copolymer is generally observed to have the chemical potential close to the lowest unoccupied molecular orbital,@footnote 1@ with a band gap of about 6 eV.@footnote 2@ PMVC exhibits a much greater band gap, with the Fermi level placed roughly mid way within the highest occupied to lowest unoccupied molecular orbital (HOMO-LUMO) gap. The implications of these differences in electronic properties will be discussed, in particular with regard to electron-phonon coupling.@footnote 3@ @FootnoteText@ @footnote 1@Jaewu Choi, P.A. Dowben, S. Pebley, A. Bune, S. Ducharme, V.M. Fridkin, S.P. Palto, N. Petukhova, Phys. Rev. Lett. 80 (1998) 1328-1331@footnote 2@Chun-gang Duan, W.N. Mei, J.R. Hardy, S. Ducharme, J. Choi, P.A. Dowben, Europhys. Lett. 61 (2003) 81-87@footnote 3@Luis G. Rosa, Ya.B. Losovyj, J. Choi, and P.A. Dowben, J. Physical Chemistry B 109 (2005) 7817-7820.

2:20pm **SS+EM-WeA2 Energetics of Metals Adsorption on Polymers: Calorimetric Studies***, **J.F. Zhu**, S.F. Diaz, P. Goetsch, J.J.W. Harris, C.T. Campbell,* University of Washington

We report here the first calorimetric measurement of any metal adsorption energy onto any polymer surfaces wherein the sticking probability of the metal also was measured. The heat of adsorption and sticking probability were measured for Pb and Ca gas atoms adsorbing onto clean poly(methyl methacrylate) (PMMA) and electron-irradiated PMMA. The PMMA film was spin coated directly onto the heat detector, a pyroelectric polymer foil (polyvinylidene fluoride - PVDF) precoated on both sides with metal thin films to serve as electrodes. This provides a detector sensitivity of ~450 V/Jabs with a pulse-to-pulse standard deviation of 1.2 kJ/mol and an absolute accuracy within 2%. The Pb atoms interact very weakly with the outgassed pristine PMMA surface, with a sticking probability of 0.02 ± 0.02. They deposit a heat into the PMMA of 12.7 ± 0.7 kJ per mole of dosed Pb, independent of Pb exposure up to 10 ML. This is slightly less that would be expected even if no Pb atoms stuck to the PMMA, but if they completely thermally accommodated to the substrate temperature during their collisions with the surface. This proves that thermal accommodation is incomplete, highlighting the weakness of the Pb - PMMA interaction. Calcium interacts with pristine PMMA much more strongly, with an initial sticking probability of ~0.5 and an initial heat of adsorption above 240 kJ/mol. Damaging the PMMA surface with electrons causes an increase in reactivity with Pb, as evidenced by increases in the initial heat of adsorption up to 134.0 ± 0.7 kJ/mol and the initial sticking probability up to 0.51 ± 0.01. Both increase with increasing coverage toward values expected for Pb adsorption onto bulk Pb.

3:00pm **SS+EM-WeA4 Contrasting the Assembly and Molecular Architecture of N-heteroaromatic Molecular Films on Ag(111): ACA vs. INA***, **H. Li**, B. Xu, D. Evans, J. Reutt-Robey,* University of Maryland at College Park

Monolayer films of isonicotinic acid (INA) and 9-acridine carboxylic acid (ACA) were prepared by physical vapor deposition and investigated with complementary scanning tunneling microscopy (STM) and spectroscopy (XPS, RAIRS) under UHV conditions. These N-heteroaromatic acids offer the same H-bonding motifs, but varied sizes and electrostatic properties, which should impact film architecture. In the monolayer regime, STM images reveal that both molecules readily assemble at room temperature into ordered "2-D" structures with typical domain sizes exceeding 100 nm for INA and 1000 nm for ACA. Differences between the domain structures (INA domains being more anisotropic and with much sharper (molecularly smooth) boundaries) are related to differences in their intermolecular forces. We propose structural models consistent with high resolution STM images and test these structural models with detailed spectroscopic measurements. XPS studies of N 1s and O 1s core level shifts identify a predominant H-bonding motif based upon N head-to- carboxyl tail interaction, in agreement with the proposed structural model. Surface infrared measurements of INA molecular films detect a pronounced out-of-plane aromatic H bending mode at 858 cm@super -1@, and an intensity analysis determines the aromatic plane to be tilted by ~20° from the substrate plane. The proposed structural model for ACA involves an arrangement of ACA molecules with greater and alternating tilt angles, which we are presently testing with infrared experiments. We will account for these distinct molecular film architectures with the differences in the intermolecular forces and discuss the generality of these effects.

3:20pm **SS+EM-WeA5 Intermolecular Interactions in Ultrathin Organic Films*, N.V. Richardson,*** University of St Andrews, UK **INVITED**

Across the complexity of molecular systems, which have now been studied in great detail at well-defined, single crystal surfaces, particularly metal surfaces, there is a great variety in the strength, nature and significance of the interamolecular interactions which are possible. It is the balance of these interactions with the adsorbate/substrate interaction that is a key determinant of the two dimensional order, which can be achieved in the system. In the simplest cases, the interaction may be limited to Van der Waals' attractions balanced by local steric repulsion, while in more complex cases, highly directional H-bonding interactions can dominate the interadsorbate interaction. In the case of adsorption on relatively soft metals such as copper, silver and gold the strength of the interaction of the molecule with the surface atoms can be comparable with or even greater than that between the surface metal atoms, this can lead to the formation of highly ordered 2D adsorbate structures involving significant translocation of metal atoms, most likely in the form of metal adsorbate complexes, and consequential large scale restructuring of the surface. In this presentation, some examples of the relevance of intermolecular interactions in determining adsorbate structures in the sub-monolayer to monolayer regime will be given based on our studies of molecules ranging from aromatic hydrocarbons, through alkane and fluoroalkane thiols to simple biomolecules, such as amino acids and nucleic acid bases. In a somewhat more detailed description of two adsorbate-substrate systems, the role of a two dimensional monolayer in templating a novel three dimensional bulk structure will be described and, in the other example, the ability of a racemic mixture of adsorbing molecules to exploit intermolecular interactions leading to chiral phase segregation will be demonstrated.

4:00pm **SS+EM-WeA7 Conformational Changes and Chiral Ordering in Adsorbed Molecular Layers Investigated by Time-resolved STM*, S. Weigelt*[1]***, *C. Busse, L. Petersen, T.R. Linderoth, E. Rauls, B. Hammer, K.V. Gothelf, F. Besenbacher,* University of Aarhus, Denmark

Detailed understanding of intermolecular interactions and molecular dynamical processes is required to control, and ultimately exploit, molecular self-assembly on surfaces. Recently, self-assembled structures formed from molecules that become chiral once confined to the surface plane have received particular attention. In this contribution we investigate a family of organic molecules that surprisingly can switch chirality as well as switch between chiral and non-chiral forms after adsorption by undergoing spontaneous conformational changes. The molecules (oligo-(phenylene-ethynylene)'s) consist of a central benzene ring with two or three ethynylene spokes each terminating in a tert-butyl substituted salicylaldehyde moiety. Upon vapour deposition onto the Au(111) surface under UHV conditions, the molecules assume different surface conformers, distinguishable in STM images by the positions of the tert-butyl groups relative to the molecular backbone. Some of these surface conformers are chiral and the chirality of the conformers and the chirality of the assumed molecular tiling patterns are highly correlated. The correlation is enabled by an intra-molecular switching mechanism, allowing the adsorbed molecules to flip between different surface conformers (and hence between different chiral forms) by rotating their end groups around the axis of the ethynylene spoke. This chiral switching enable the molecules to form extended homo-chiral domains by dynamically accommodating to the chiral template found at domain perimeters. We have performed a detailed investigation of this intra-molecular dynamic process by monitoring the surface with time-resolved STM at substrate temperatures in the interval 150-220K. The rate for the conformational change follows an Arrhenius dependence on temperature with activation energy ~0.3 eV. Theoretical modeling is currently being performed to illuminate this novel intra-molecular dynamical process.

4:20pm **SS+EM-WeA8 Resonant Soft X-Ray Emission and Inelastic X-Ray Scattering Studies of Electronic Structure in Metal Phthalocyanines***, Y. Zhang, S. Wang, L. Plucinski,* Boston University*; J.E. Downes,* Victoria University of Wellington, New Zealand*; C. McGuinness,* Trinity College Dublin, Ireland*; P.A. Glans, T. Learmonth, **K.E. Smith**,* Boston University

We report synchrotron radiation-excited resonant soft x-ray emission (SXE) spectroscopy and resonant inelastic x-ray scattering (RIXS) studies of the electronic structure of thin films of metal phthalocyanines (M-Pc).@footnote 1@ SXE measures the element-resolved partial density of states (PDOS) in materials. At a core level resonance, SXE measures the non-ionized PDOS associated with specific chemical sites. Furthermore, RIXS features can be observed which are related to low energy excitations in the system. We discuss the application of SXE and RIXS in the study of M-Pc. Our results are in excellent agreement with theory, but differ significantly from previously published experiments. The films were found to be highly susceptible to beam damage. We successfully circumvented this effect by continuous film translation during measurement. Resonant SXE spectra from undamaged Cu-Pc samples show spectral features near the Fermi level (E@sub F@) that, although predicted, have not previously been observed.@footnote 2@ We have also studied vanadium oxide phthalocyanine (VO-Pc), and in addition to measuring the element resolved PDOS, have observed dipole forbidden V 3d - V 3d* and O 2p - V 3d* charge transfer transitions across the band gap. The ability to accurately measure states near E@sub F@ is significant, as is the discovery that many SXE studies of organic semiconductors are dominated by beam damage effects. @FootnoteText@ @footnote 1@ Supported in part by the ACS PRF, by NSF DMR-0304960, and by DOE DE-FG02-98ER45680. The spectrometer system is funded by U.S. ARO DAAD19-01-1-0364 and DAAH04-95-0014. Experiments performed at the NSLS which is supported by the U.S. DOE, Divisions of Materials and Chemical Sciences.@footnote 2@ J.E. Downes, C. McGuinness, P.-A. Glans, T. Learmonth, D. Fu, P. Sheridan, and K.E. Smith, Chem. Phys. Lett. 390, 203 (2004).

4:40pm **SS+EM-WeA9 Effects of Incident Kinetic Energy on the Nucleation and Morphological Evolution of Organic Thin Films***, A.S. Killampalli, T.W. Schroeder, **J.R. Engstrom**,* Cornell University

The deposition and growth of thin films of organic materials differs fundamentally from that of the more conventional inorganic materials. A key difference involves the presence of strong covalent and ionic bonding in the latter class of materials, whereas organic materials are often bound by rather weak dispersion forces. As a consequence, considerable promise exists in the use of energy tunable molecular beams for the deposition of organic thin films, as incident species with energies on the order of a few eV may produce substantial changes in the growth habit. We have been examining the deposition of pentacene thin films using a supersonic molecular beam source producing hyperthermal (E@subi@ = 1.4 - 10.6 eV) kinetic energies. In both the monolayer and multilayer regimes of growth of pentacene on SiO@sub2@ we find that as E@subi@ is increased from 1.5 to 6.7 eV, the growth rate at a fixed incident flux decreases, consistent with trapping-mediated adsorption. In the monolayer regime the data is well explained by nucleation theory, where the critical island size is 4.5 ± 1.3. The situation is more complex in the multilayer regime - here the decrease in the rate is less than that observed in the monolayer regime, and at sufficiently large E@subi@ (> 4 eV), the rate of deposition in the multilayer regime exceeds that in the monolayer regime by about a factor of 3. The evolution of surface roughness provides additional clues as to the dynamics of growth in the multilayer regime. For all incident kinetic energies, the growth exponent, @beta@, is greater than 0.5, indicative of rapid roughening. Our results demonstrate clearly that the morphological evolution of organic thin films can be modified substantially at high incident kinetic energies.

5:00pm **SS+EM-WeA10 Para-Sexiphenyl Thin Films Grown by Hot Wall Epitaxy on KCl(001) Substrates*, A.Yu. Andreev*,** *A. Montaigne,* University Linz, Austria*; G. Hlawacek,* University of Leoben, Austria*; T. Haber, R. Resel,* Graz University of Technology, Austria*; H. Sitter,* University Linz, Austria*; C. Teichert,* University of Leoben, Austria

Para-sexiphenyl (p-6P) is a blue emitting organic semiconductor widely investigated for optoelectronic applications. Especially, p-6P thin films grown on mica(001) and KCl(001) substrates show large morphological, electrical and optical anisotropy, which makes them attractive for nano-scale optoelectronic and photonic devices. In this work, we use Atomic Force Microscopy (AFM) and X-Ray diffraction (XRD) to study the growth of p-6P on crystalline KCl substrates, in order to find the process controlling parameters. It is shown that the growth process of p-6P on KCl(001) is quite complex and can be divided preliminary in two steps. The initial growth

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[1] **Morton S. Traum Award Finalist**

stage is characterized by the formation of the long needle-like crystallites build of "laying" molecules (as shown by XRD), generating a rectangular network in accordance with substrate surface symmetry. If the surface coverage increases, terraced crystalline mounds composed of upright standing molecules start to develop between the needles. These mounds are clearly formed due to repeated 2D nucleation of p-6P molecules. Consequently, all terraces found are in average about 2.6 nm high, which corresponds to one monolayer of standing p-6P molecules. Further, growth is characterized by a coexistence of the constantly growing needles and mounds, whereby the last ones cover finally almost the whole surface between the needles. By means of phase imaging in AFM tapping mode, it could be clearly demonstrated that both needle-like crystallites and flat terraced mounds grow directly on the substrate surface, i.e., there is no wetting layer formed during the deposition of p-6P on KCl(001).

Surface Science

Room 200 - Session SS1-WeA

Surface Structure and Morphology Modification

Moderator: P.F. Lyman, University of Wisconsin-Milwaukee

2:00pm **SS1-WeA1 Structure and Reactivity of Nanoscale Faceted Surfaces***, **T.E. Madey**, I. Ermanoski, H. Wang, W. Chen, A.S.Y. Chan, E. Loginova, N.M. Jisrawi,* Rutgers University*; W. Swiech,* University of Illinois at Urbana-Champaign **INVITED**

Many planar metal surfaces that are rough on the atomic scale, such as fcc Ir(210), hcp Re(12_31), NiAl(111) and bcc W(111), are morphologically unstable when covered by monolayer films of oxygen, or of certain metals: they become "nanotextured" when heated to elevated temperatures. Faceting occurs when an initially planar surface converts to a "hill and valley" structure, exposing new crystal faces of nanometer scale dimensions. Faceting is driven by surface thermodynamics (anisotropy of surface free energy), but controlled by kinetics (diffusion, nucleation). We report here on the relations between structure, reactivity and electronic properties of nanoscale faceted surfaces. Measurements include STM, LEED, TPD, low energy electron microscopy (LEEM) and soft x-ray photoemission (SXPS) using synchrotron radiation. For example, annealing oxygen-covered Re(12_31) gives a sequence of faceted surfaces ranging from from long sawtooth ridges, to complex structures exposing up to 5 different facets. Surface reactivity of O-covered Re is sensitive to facet structure. Oxygen-faceted NiAl(111) is covered by an alumina "skin". Annealing O-covered Ir(210) generates nanoscale pyramids with {311} and (110) facet orientations; average pyramid sizes 5 to 15 nm are controlled by annealing T. Oxygen can be completely removed at low T (by exposing to H@sub2@, to form H@sub2@O) thus creating a clean, faceted surface that is stable to 600K. Faceted Ir is a template for studies of energy-related surface reactions whose rates are sensitive to atomic structure and/or nanoscale (facet) size effects, including decomposition of H@sub2@, C@sub2@H@sub2@ and NH@sub3@. We will discuss structural and electronic properties of the surfaces, nucleation and growth of facets, implications for catalysis, and potential of faceted substrates as nanotemplates for nanoscale cluster growth. Experimental results are compared to theory. @FootnoteText@ @footnote 1@ supported by DOE - BES.

2:40pm **SS1-WeA3 Atomistic Reasons for the Oxygen Induced Step Bunching on Rh(553)***, J. Gustafson, A. Resta, A. Mikkelsen, R. Westerstrom, **J.N. Andersen**, J. Weissenrieder, E. Lundgren,* Lund University, Sweden*; F. Mittendorfer, G. Kresse,* Universität Wien, Austria*; X. Torelles,* Institut de Ciencia de Materials de Barcelona (C.S.I.C), Spain*; S. Ferrer,* ERSF, France*; N. Kasper,* Max-Planck Institut f@um u@r Metalforschung, Germany*; M. Schmid, P. Varga,* Technische Universität Wien, Austria

One of the most fundamental gas-surface interactions is that between oxygen and metal surfaces. Many studies on low index single crystal surfaces have led to an atomic scale understanding of the possible dissociation pathways for the oxygen molecule and the adsorption sites of O-atoms and molecules on such flat surfaces. Oxygen interaction with vicinal surfaces - which due to their high step density better model small metal particles typically used in catalysis - has received much less attention. Similarly only few studies have been performed under conditions - higher temperatures and/or higher oxygen pressures - where strong rearrangements of the substrate surface may occur. Accordingly an atomic level understanding of the oxygen-surface interaction under conditions - material, pressure, and temperature - typical for instance for catalysis is still in its infancy. Here we present an extensive study, using a multi-method approach, of the initial oxidation of Rh(553), a surface vicinal to (111) with a large density of steps. Our results show that the surface undergoes step bunching when exposed to oxygen, forming lower index facets. At a pressure of about 10-6 mbar and a temperature of 400Â°C this leads to (331) facets with 1D-oxide chains along the steps, co-existing with (111) facets. Increasing the pressure and temperature further results in (111) facets only, covered by a O-Rh-O surface oxide as found on Rh(111).@footnote 1@ @FootnoteText@@footnote 1@ J. Gustafson et al., Phys. Rev. Lett. 92 (2004) 126102.

3:00pm **SS1-WeA4 Atomic-Scale Visualization of Surface Alloys: Sb/Au(110)***, **S.S. Parihar**, V.L. Shneerson, R. Fung, H.T. Johnson-Steigelman, E.D. Lu, D.K. Saldin, P.F. Lyman,* University of Wisconsin-Milwaukee

Surface x-ray diffraction (SXRD) allows quantitative, high-resolution determinations of surface structure via @chi@@super 2@ refinement of a model structure to the observed data. However, the most difficult step in this process is often generating model structures to refine. While this is often possible based, e.g., on chemical intuition, a model-independent method of generating accurate starting structures is sorely needed. We have developed an iterative algorithm to supply the phases, normally not accessible to experiment, from data that are oversampled (relative to the Nyquist frequency of the normal dimensions of the selvedge) along the crystal truncation rods. The algorithm alternately satisfies known constraints of these oversampled data in real and reciprocal space, and incorporates knowledge of the bulk structure, to progressively determine the surface structure factor phases. An inverse Fourier transform then constructs an "image" of the atomic contents of a unit cell of the selvedge.@footnote 1@ We have discovered a rich sequence of Sb-induced reconstructions on Au(110). A c(2x2) appears at 0.5 ML, changing continuously to a (@sr 3@x@sr 3@)R54.7° structure at higher Sb coverages; finally, a p(5x6) structure emerges for several ML Sb deposition. We have applied our novel SXRD algorithm to these surfaces to directly visualize the Sb and Au atomic locations, and thereby solve these structures. This breakthrough affords an automated, model-independent method of determining unknown structures of the outermost few atomic layers of a crystal surface. @FootnoteText@ @footnote 1@ P.F. Lyman, V.L. Shneerson, R. Fung, R.J. Harder, E. D. Lu, S.S. Parihar, and D.K. Saldin, Phys. Rev. B 71, 081402(R) (2005).

3:20pm **SS1-WeA5 Adatom-Pair Chain Structures: Metastable Precursors to Island Formation on the Ge-Si(100) 2xN Alloyed Surface***, **K.J. Solis**, L.R. Williams,* University of New Mexico*; B.S. Swartzentruber,* Sandia National Laboratories*; S.M. Han,* University of New Mexico

We have identified that adatom pairs are the main transport adspecies on the 2xN SiGe wetting layer, using polarity-dependent scanning tunneling microscopy. These adatom pairs form chevron-like, conjugated chains on the SiGe alloy surface, ranging in length from 1 to approximately 10 units of adatom pairs. The adatom-pair chains exhibit kinked and straight segments. We measure a kink-to-straight ratio of 2:1, surpassing the 1:1 ratio predicted from random chain configurations. Substrate-mediated-strain interactions are likely to render the kinked segments energetically favorable. These adatom-pair chains convert to compact islands at elevated temperatures, suggesting that they are the main precursor to island formation on the SiGe wetting layer. We use a pattern-recognition algorithm to distinguish adatom pairs from compact islands in dual-polarity images, and measure the conversion rate from 90 to 150 °C to extract the activation barrier. The authors acknowledge support from NSF CAREER (DMR-0094145) and ARO (W911NF-05-1-0012). Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

3:40pm **SS1-WeA6 Growth and Subsequent Decomposition Kinetics of Very Thin Oxide on Si(001) Surface Studied by Real-Time RHEED Combined with AES***, **S. Ogawa**, Y. Takakuwa,* IMRAM, Tohoku University, Japan

In order to clarify the rate-limiting reaction of layer-by-layer oxidation on Si surfaces, the growth and subsequent decomposition kinetics of very thin oxide on the Si(001)2X1 surfaces were investigated by a real-time monitoring method of Reflection High Energy Electron Diffraction combined with Auger Electron Spectroscopy (RHEED-AES) to measure the oxide coverage and surface structure/morphology simultaneously. The 1@super st@ oxide layer was grown by two oxidation manners of Langmuir-type adsorption at 500°C and two-dimensional (2D) oxide island growth at 690°C under 2X10@super -6@ Torr of O@sub 2@ pressure. No progress of 2@super nd@ oxide layer growth was observed after completion of 2D oxide island growth, although the 2@super nd@ oxide layer can grow gradually following the Langmuir-type adsorption. It is difficult to interpret the observed difference in the 2@super nd@ oxide layer growth kinetics, because the observed tendency is contrary to thermal activation from 500°C to 690°C. Furthermore, thermal decomposition of the oxide grown at 690°C is more difficult than that grown at 500°C. Thus the rate of 2@super nd@ oxide layer growth is closely concerned with that of decomposition. The reason for the correlation is quantitatively discussed with the time of void nucleation measured as a function of oxidation time after completion of 1@super st@ oxide layer growth.

4:00pm **SS1-WeA7 Surface Morphologies produced by Oxygen Etching of Stable and Unstable Si Surfaces*, A.A. Baski*,** *M.L. Willis, J.W. Dickinson, J.L. Skrobiszewski,* Virginia Commonwealth University

We have used scanning tunneling microscopy (STM) and atomic force microscopy (AFM) to study the morphologies produced on Si surfaces by oxygen etching. When Si surfaces are heated to between 700 and 850°C and exposed to O@sub 2@, the simultaneous processes of etching and oxide nucleation can significantly modify the surface structure. As etching removes surface atoms, oxide-induced pinning sites can modify the step structure and lower-energy facet planes can be exposed. In these experiments, a range of O@sub 2@ exposures (50 to 400 L) have been explored for surface orientations that include: (001), (111), (113), (5 5 12), and (112). All of these orientations except Si(112) form stable, clean surface reconstructions. At lower exposures and temperatures, oxygen etching on all of the surface orientations leads to step retraction and the appearance of islands on terraces and at step edges. These islands are presumably due to oxide-induced pinning sites that remain as the surrounding area is etched. The high-index (113) and (5 5 12) surfaces show significantly less terrace etching and enhanced island nucleation along step edges. At higher exposures and temperatures, fewer kinetic limitations are present and the resulting morphologies reflect the stability of surface planes. The (001), (111), and (113) surfaces remain relatively flat with monolayer islands that reflect the surface symmetry. In contrast, the less thermodynamically stable (5 5 12) surface is etched to expose linear sawtooth structures composed of (111) and (113) planes. Similarly, the unstable (112) surface shows dramatic restructuring with the formation of sawtooths composed of (111), (113), (225), and/or (337) planes. Short (112) segments are also sometimes observed, indicating that adsorbed oxygen may stabilize this otherwise unstable orientation. Further studies are in progress to examine exposures above 1000 L where a steady-state morphology should exist.

4:20pm **SS1-WeA8 Cyclic Transformation of 1-D Structures during Homoepitaxy of Si(5 5 12)-2x1*, H. Kim*,** *Y. Cho, J.M. Seo,* Chonbuk National University, Korea

In the homoepitaxy of Si(5 5 12)-2x1 at a finite temperature, 500 C, it has been found by STM that Si overlayer grows in the layer-by-layer fashion and there are three distinct stages, such as dimer-filling, faceting, and valley-filling stages, for recovering Si[5 5 12]-2x1. In each transformed stage, the number of dangling bonds as well as 1-D symmetry with three kinds of reconstructed features, such as honeycomb(H) chain, tetramer(T) row, and dimer-facing-adatoms(D/A) row, are always preserved on the reconstructed surface under a quasi-equilibrium state with deposited Si atoms. The simple rule observed in this 1-D structural transformation is as follows: A honeycomb(H) chain is broken into a tetramer(T) row by the compressive stress, a T row is split to a dimer-facing-adatoms(D/A) row by the tensile stress, and a D/A row is transformed to a H chain by two adsorbed-dimers. Only in the last transformation, the center of 1-D feature shifts in the direction of [-6-6 5] by 3.04 A. It takes only 28 atoms per unit cell to recover the identical, planar and reconstructed Si(5 5 12)-2x1. The reason why such an amount of Si atoms for recovering the original surface is much smaller than that of surface atoms involving in the reconstruction of Si(5 5 12) is in the fact that the exact growth-direction is not along [5 5 12] but along [-1-1 2]. One-cycle of homoepitaxy is completed when seven (111) double-step edges of a unit-cell of Si(5 5 12)-2x1 are filled with two dimers respectively, and results in the effective height increment of 1.36 A and horizontal shift of 3.04 A toward [-6-6 5].

4:40pm **SS1-WeA9 Intrinsic Vacancy-Induced Nanostructure of Al@sub 2@Se@sub 3@: Another New Silicon Compatible Chalcogenide Based Semiconductor*, C.Y. Lu*,** *J.A. Adams, D.A. Schmidt, X. Li, Q. Yu, M.A. Olmstead, F.S. Ohuchi,* University of Washington

Adding new functionalities, such as magnetism and spintronics, to existing silicon-based technology requires combining different crystalline materials with silicon through heteroepitaxy. One intriguing class of materials that is both structurally and chemically compatible with silicon is the Group-III-Selenide semiconductors, such as Ga@sub x@Se@sub y@ and Al@sub x@Se@sub y@. These materials have intrinsic vacancies that influence the film morphology and resultant crystalline structure during the heteroepitaxial growth, and may also be used to host dissimilar atoms, such as magnetic transition metals, to add unique functionalities. We report here in-situ scanning tunneling microscopy and photoelectron spectroscopy of aluminum-selenide (Al@sub x@Se@sub y@) heteroepitaxy on Si(111)-7x7 and As-terminated Si(100). Unlike Ga@sub x@Se@sub y@, which crystallizes into either a layered GaSe or defected zinc-blende Ga@sub 2@Se@sub 3@, Al@sub x@Se@sub y@ exhibits only one bulk structure: defected wurtize. We find heteroepitaxy of Al@sub x@Se@sub y@ on Si(111) results in hexagonal Al@sub 2@Se@sub 3@, likely wurtzite, but defected zinc-blende Al@sub 2@Se@sub 3@ is initially formed on As-terminated Si(100). The morphology of Al@sub 2@Se@sub 3@/Si(111) consists of triangular nanodots with single orientation, in contrast to the mixed orientation of layered GaSe on Si(111). For Al@sub 2@Se@sub 3@/Si(100):As, we observe oriented nanowire structures at low coverage, similar to low coverage Ga@sub 2@Se@sub 3@/As:Si(100)nanowires;@footnote 1@ hexagonal crystalline islands nucleate after 2-3 bilayers. In these first 2-3 layers, the spiral vacancy arrangement unique to the wurtize structure is altered to a linear array by the symmetry of Si(100)substrate. We propose that different symmetry and bonding of the substrate surfaces induces different configurations of vacancies, resulting in the distinct surface nanostructures. @FootnoteText@ @footnote 1@T. Ohta et al., Phys. Rev. Lett. 94, 116102 (2005).

Surface Science
Room 203 - Session SS2-WeA
Reactions on Nanoclusters

Moderator: I. Chorkendorff, Technical University of Denmark

2:00pm **SS2-WeA1 Physical and Chemical Properties of Model Catalysts Prepared by Size-Selected Cluster Deposition*, T. Wu*,** *S. Lee, C. Fan, W. Kaden, S.L. Anderson,* University of Utah

In surface chemistry, one of the most important goals is to understand the relationship between surface structure and catalyst reactivity, especially at an atomic level. An interesting aspect of this field is the effect of particle size in supported catalysts, i.e., how cluster size affects the physical properties of the surface, as well as the activity for specific reactions. In our lab, model gold, iridium, and palladium catalysts were prepared by deposition of size-selected metal clusters on well defined oxide surfaces, and characterized by a combination of X-ray photoelectron spectroscopy (XPS), ion scattering spectroscopy (ISS), temperature-programmed desorption, and pulse-dosing mass spectrometry. Activity is strongly size-dependent. For example, in reaction of hydrazine on Ir/alumina model catalysts, both activity, and the distribution of products change dramatically with cluster size. Strong dependence on size is also seen for CO oxidation.

2:20pm **SS2-WeA2 Probing the Chemical Reactivity of Oxide-Supported Pd Nanoparticles with STM***, J. Zhou,* ***A.P. Baddorf****, S.V. Kalinin, S.H. Overbury, D.R. Mullins,* Oak Ridge National Laboratory

Oxide-supported metal nanoparticles play a central role in current heterogeneous catalysis. They may exhibit unique catalytic properties that can be tuned by particle size and structure as well as by choice of oxide substrate. However, there is still a need to understand the origins of catalytic activity of metal/metal-oxide interfaces at the atomic scale. We report scanning tunneling microscopy (STM) studies of supported Pd nanoparticles evaporated on a rutile TiO@sub 2@ (110) single crystal surface in ultrahigh vacuum as a model catalytic system. A range of particle sizes with narrow size distributions was prepared by varying Pd coverage, substrate growth and post-annealing temperatures. Electronic properties of the particles and adjacent substrate were determined with I-V and dI/dV spectroscopies. The surface chemistry of supported Pd particles was explored for reactive gases such as O@sub 2@, CO and benzene between 20 and 300 K. Images of specific particles are compared before and after in situ exposures. Research was sponsored by the Laboratory Directed Research and Development Program of ORNL, managed by UT-Battelle, LLC for the U. S. DOE under Contract DE-AC05-00OR22725.

2:40pm **SS2-WeA3 Structure and Reactivity of Metal Clusters***, **H.J. Freund,*** Fritz-Haber-Institute of the Max-Planck-Society, Germany **INVITED**

Model catalyst systems have been prepared by growth of metal nano-aggregates on thin well-ordered oxide films of alumina and silica. These systems lend themselves to structural and morphological characterization via scanning probe microscopies and transmission electron microscopy and bridge to a certain extent the materials gap between metal single crystal studies and the investigation of real catalyst samples. It is possible to infer direct structure-reactivity relations when simple reactions of small molecules are studied. We have applied a variety of surface sensitive techniques, both under ultrahigh vacuum as well as under ambient conditions to relate observations from surface science to those in catalysis under realistic gas pressure conditions. Examples are presented.

3:20pm **SS2-WeA5 The Active Structure of Supported Au Catalysts***, **M.S. Chen**, Z. Yan, Y. Cai, W.T. Wallace, X.F. Lai, D.W. Goodman,* Texas A&M University

The high catalytic activity of gold clusters on oxides has been attributed to structural effects, including particle thickness and shape, metal oxidation state, as well as support effects. The best catalytic performance of supported Au particles was found for clusters with sizes of 2~3 nm. For Au clusters supported on TiO2(110), the unique properties have been associated with Au structures two atomic layers in thickness based on STM and kinetic measurements (M. Valden, X. Lai, D. W. Goodman, Science 281, 1647 (1998)), and confirmed by our recent results. Specifically, we have synthesized well-ordered Au monolayers [(1x1)] and bilayers [(1x3)] that completely wet (cover) the oxide support [a titanium oxide monolayer film grown on the Mo(112) surface] (M. S. Chen, D. W. Goodman, Science 306 (2004) 252.). Kinetic measurements for CO catalytic oxidation show that the Au bilayer structure is significantly more active (by more than an order of magnitude) than the monolayer strucuture, and is approximately 45 times higher than that reported for the most active high-surface-area Au/TiO2 catalysts. These specific rates clearly indicate that bilayer Au is the active structure for CO oxidation. These results eliminate particle shape and direct support effects as significant contributions to the special catalytic properties of nano-sized Au clusters.

3:40pm **SS2-WeA6 Neutralization of Low Energy Li Ions Scattered from Au Nanoclusters***, **G.F. Liu,*** University of California, Riverside*; Z. Sroubek,* Czech Academy of Sciences*; J.A. Yarmoff,* University of California, Riverside

Charge exchange during the scattering of low energy (0.5-10 keV) alkali ions provides a sensitive measure of the confined quantum states of nanomaterials. In earlier work, we showed that the neutralization of Na@super +@ scattered from Au nanoclusters correlates with the presence and position of the confined states.@footnote 1@ In this work, we scatter Li ions from Au nanoclusters grown on TiO@sub 2@(110). The neutralization probability of the Li singly scattered from the Au nanoclusters is measured with time-of-flight spectroscopy. Au nanocrystals grown on TiO@sub 2@(110) possess unique catalytic properties, which depend on the cluster size. The size of the clusters is determined by the amount of Au deposited and the surface temperature, and increases with the amount deposited. The neutral fraction was found to have a maximum at ~0.2 ML Au coverage, which is consistent with the maximum seen for the catalytic activity.@footnote 2@ This provides clear evidence that the ion scattering is probing the same states that are responsible for unique properties of these materials. When additional Au is deposited, the neutral fraction first drops to a minimum (at ~10 ML Au), and then increases to the bulk Au value. This shows that ion scattering is able to monitor the formation of the conduction band as a transition is made from isolated clusters to a continuous film. In addition, the dependence of the neutral fraction on the ion exit angle and energy was investigated. In order to better correlate the dependence of the cluster sizes on the neutral fraction, future experiments will involve Li and Na ions scattered from size-uniform nanoclusters grown by chemical synthesis. @FootnoteText@ @footnote 1@G. F. Liu, Z. Sroubek, and J. A. Yarmoff, Phys. Rev. Lett. 92, 216801 (2004). @footnote 2@M. Valden, X. Lai, and D.W. Goodman, Science 281, 1647 (1998).

4:00pm **SS2-WeA7 Growth and Reactivity of Bimetallic Pt-Rh Nanoclusters on Titanium Dioxide**, *S. Ma,* Brookhaven National Laboratory*; J.S. Ratliff, J.B. Park, **D.A. Chen**,* University of South Carolina

Bimetallic Pt-Rh nanoclusters have been grown on rutile TiO@sub 2@ by vapor deposition under ultrahigh vacuum conditions. Low energy ion scattering (LEIS) experiments show that Pt tends to segregate to the surface of the nanoclusters, regardless of whether Rh is deposited on top of Pt or Pt is deposited on top of Rh. Pt diffusion into the clusters occurs readily at room temperature and is only slightly slower when the deposition temperature is decreased to 220 K. Scanning tunneling microscopy (STM) experiments indicate that for 2 monolayers of Pt deposited on 2 monolayers of Rh, the resulting clusters have an average height of 0.9 nm and diameter of 5 nm. Although heating to 850 K significantly increases the Pt-Rh cluster size (1.3 nm height, 7 nm diameter), LEIS experiments indicate that the clusters become completely encapsulated with TiO@sub 2@ at temperatures above 700 K. In situ STM experiments demonstrate that during the deposition of Pt on Rh clusters, existing clusters grow bigger, new Pt clusters are nucleated, and many growing Pt-Rh clusters merge with neighbors to form larger clusters. The reaction of NO on pure Pt or Rh clusters results in production of N@sub 2@ as well as desorption of NO. However, NO chemistry on bimetallic Pt-Rh clusters is qualitatively different since a new product, N@sub 2@O, is also observed. The reduction of NO with CO to produce N@sub 2@ and CO@sub 2@ does not occur on pure Pt or Rh clusters but is observed on the bimetallic Pt-Rh clusters.

4:20pm **SS2-WeA8 Reactive-Layer-Assisted Deposition (RLAD) of TiO@sub 2@ Nanoparticles on Au(111) Studied by STM and XPS***, **Z. Song**,* Columbia University*; J. Hrbek,* Brookhaven National Laboratory*; R.M. Osgood,* Columbia University

TiO@sub 2@ nanoparticles have been prepared by reactive-layer-assisted deposition (RLAD), in which Ti atoms are initially deposited on a multilayer of H@sub 2@O (or NO@sub 2@) grown on a Au(111) substrate at temperature <100 K. The chemical, structural and electronic properties of these oxide nanoparticles were studied by XPS, STM and STS. Specifically, ~1nm diameter TiO@sub 2@ particles formed with an H@sub 2@O reactive layer were obtained after raising the substrate temperature to 300K. Use of NO@sub 2@ reactive layers yields TiO@sub 2@ nanoparticles (~1nm at 300K) with NO@sub 3@ radicals decorating their surfaces at temperatures bellow 500K. Further annealing induces the desorption of N-containing species and leaves behind flat TiO@sub 2@ rutile and anatase particles (~5nm after being annealed to 700K) with various facets. STS studies showed different electronic structures for different TiO@sub 2@ particle sizes. This UHV compatible method for preparing well-defined TiO@sub 2@ nanoparticles can be used in molecular-level studies of reaction mechanisms of photocatalytic processes on TiO@sub 2@ nanoparticle surfaces.

5:00pm **SS2-WeA10 Bimodal Pd Cluster Growth on the Reduced SnO2 (101) Surface***, **Kh. Katsiev**, M. Batzill, U. Diebold,* Tulane University

Tin oxide is a solid state gas sensor for detection of combustible and toxic gases. Its sensitivity and selectivity can be enhanced by catalytically active dopants, such as Pd. We have studied the growth of Pd on the SnO2 (101) surface in the sub-monolayer regime in order to gain new insights into the gas sensing mechanism. The SnO2 substrate exhibits a 1x1 bulk termination, with the surface tin atoms in a reduced Sn2+ charge state. This reduction of the surface Sn atoms results in the formation of a Sn-5s derived surface state. Upon deposition of Pd onto SnO2 (101), bimodal cluster growth was observed. For very low coverages, two-dimensional, round clusters decorate (0-10) -oriented step-edges, a behavior typical for many metal-on-oxide systems. In addition, we observe quasi one-dimensional Pd clusters growing on terraces. In both cases Pd wets the reduced tin oxide surface. The one-dimensional clusters are imaged in scanning tunneling microscopy as straight, parallel nanostructures oriented along the (-101) direction, all with the same characteristic width of 1 nm and a height of 1ML. XPS shows metallic Pd. A 0.45 eV shift in the Pd 3d core level peak position to lower binding energy occurs during the initial stages of the growth. This might be an indication of charge transfer from the Pd clusters to the substrate. Coverage-dependent UPS show that at fractional monolayer coverages, a Pd peak appears at the same position in the band gap as the Sn-5s surface state of reduced SnO2(101), indicating a possible hybridization of Sn-5s with the Pd d-band. This is the first observation of formation of one-dimensional, metallic nanowires on a wide-band gap material.

Thin Films
Room 306 - Session TF-WeA
Fundamentals of Thin Films

Moderator: M.C.M. Van De Sanden, Eindhoven University of Technology, The Netherlands

2:20pm **TF-WeA2 PECVD Silicon Nitride Nucleation Kinetics Impact on Device Scaling***, **A. Raviswaran**, P. Keswick,* Cypress Semiconductor

Plasma enhanced chemical vapor deposition of silicon nitride is a commonly used process in the microelectronics industry for etch stop and passivation layers. As the device dimensions continue to shrink along Moore's law, the silicon nitride thickness is also reduced to meet device requirements. So controlling the silicon nitride thickness and stoichiometry is critical as the gate length and contact width are affected by the thickness and etch rate of the silicon nitride layer used as etch-stop. The current study helps understand the initial stages of nucleation and growth of the PECVD silicon nitride and contributes significantly to better controlling the deposition of very thin silicon nitride layers used in device fabrication. Silicon nitride films with thickness ranging from 37 Å (deposition time of 1 sec) to 450 Å was deposited on Si wafers at 400 °C. Spectral data collected using an ellipsometer shows that as the thickness of the film increases, a transformation is observed in the spectral profile at about 200 Å thickness. AFM, SEM and cross section TEM show that the films are continuous (no 3D cluster growth) at 37 Å. In contrast to reports on LPCVD silicon nitride, the PECVD nitride deposition rate is found to increase with a reduction in deposition time and does not show an incubation time. The refractive index of these films is found to increase with a decrease in film thickness. XPS analysis shows that the thinner films are silicon rich. The 85 Å film with RI of 2.17 has a Si/N ratio of 0.947 and the 340 Å film with RI of 1.95 has a Si/N ratio of 0.928. Evaluation of hydrogen in the film by FTIR and HFS (in progress) will further help understand the impact of hydrogen on the nucleating film properties. The nucleation of a 2D Si-rich layer is attributed to high PECVD deposition rate (relative to surface diffusion) and lower bond strength of Si-H relative to N-H bonds in the reactant gases.

2:40pm **TF-WeA3 Transition Metal Diborides by CVD: Super-Conformal, Epitaxial, Diffusion Barrier, and Super-Hard Films***, **J.R. Abelson**,* University of Illinois at Urbana-Champaign **INVITED**

Transition metal diborides are metallic ceramic materials with high electrical conductivities, refractory melting temperatures, and high hardness. Despite these attractive properties, the boride compounds have been overlooked in thin film science and technology relative to the carbides and nitrides. We employ the single-source, impurity-free precursors Hf(BH@sub 4@)@sub 4@, Zr(BH@sub 4@)@sub 4@ and Cr(B@sub 3@H@sub 8@)@sub 2@ to deposit stoichiometric thin films of HfB@sub 2@, ZrB@sub 2@, and CrB@sub 2@ by chemical vapor deposition. This talk highlights recent results on film microstructure, properties, and deposition mechanisms, which are analyzed using spectroscopic ellipsometry, line-of-sight mass spectroscopy, and trench coverage. Films grown at substrate temperatures of 200-300°C are diffraction amorphous and super-conformal in deep (20:1) trenches. The conformality is a consequence of site blocking which greatly lowers the precursor sticking coefficient. HfB@sub 2@ and ZrB@sub 2@ films are excellent diffusion barriers that prevent the mixing of Cu and Si during annealing up to 600°C. At growth temperatures @>=@ 500°C the films are crystalline and adopt a strong preferred orientation, including a normal texture on SiO@sub 2@ and pseudo-epitaxy on crystalline silicon (100) and (111) substrates. The latter may be good templates for heteroepitaxial growth of GaN, as previously reported. Amorphous HfB@sub 2@ can be crystallized by annealing at temperatures @>=@ 600°C. The post annealed films have an equiaxed, nanocrystalline structure with grain diameters of < 100 Å. Such films exhibit nanoindentation hardness as high as 40 GPa, exceeding the reported bulk value of 29 GPa. We create multilayered structures by periodically introducing a flux of atomic nitrogen during growth. This creates thin mixed phase layers that are softer; the ratio of hardness to modulus can be adjusted and the overall toughness increased.

3:20pm **TF-WeA5 Sputter Deposition of Silicon Oxynitride for Waveguide Applications***, **J.G. Sandland**, A. Eshed, L.C. Kimerling,* Massachusetts Institute of Technology

Silicon oxynitride (SiON) is an ideal waveguide material because the SiON materials system provides substantial flexibility in composition and refractive index. SiON can be varied in index from that of silicon dioxide (n=1.46) to that of silicon-rich silicon nitride (n~2.3). This flexibility in refractive index allows for the optimization of device performance by allowing trade-offs between the advantages of low-index contrast systems and the benefits of high-index-contrast systems. We present sputter processing as an alternative to traditional CVD processing of SiON. We explore a co-sputtered deposition from a silicon oxide and a silicon nitride target, and reactive sputtering process from a silicon nitride target in oxygen ambient. Silicon nitride sputtered from a silicon nitride target is also investigated. Models were developed predicting the index and composition as function of deposition conditions. A materials study is provided that shows sputtered SiON to be a homogeneous material that gives good control of refractive index. Reactively sputtered SiON is shown to be Si-rich. These sputtered materials investigated for use as a core material in optical waveguides. Low loss waveguides are demonstrated for both co-sputtered and reactively sputtered depositions. Losses below 1 dB/cm are shown for co-sputtered deposition (n=1.65). These waveguide losses are then related back to our sputtering model, and silicon dangling bonds are shown to contribute to the losses in the waveguides.

3:40pm **TF-WeA6 ALD-like Deposition of High Quality SiO@sub 2@ Film at 200°C using Organic Silicon Source Gas and Highly Concentrated O@sub 3@ Gas***, **T. Nishiguchi**, N. Kameda, Y. Morikawa, M. Kekura,* Meidensha Corporation, Japan*; H. Nonaka, S. Ichimura,* National Institute of Advanced Industrial Science and Technology, Japan

One of the technical issues to be solved to fabricate a high performance flexible poly-silicon (p-Si) TFT is the development of the technique of high-quality gate dielectric (SiO@sub2@) film formation even as low as 200 ° C. Although plasma enhanced CVD using an organic silicon source / O@sub 2@ gas is now widely used, the further reduction of impurity incorporation such as carbon and OH is required. Focusing on the high reactivity of O@sub 3@ to organic molecules even at low temperature, we have carried out an ALD-like process by supplying an organic silicon source gas and highly concentrated (100%) ozone (HC-O@sub 3@) gas to a vacuum (< 1 Pa) processing chamber alternately and cyclically. The SiO@sub2@ deposition rate on Si substrate was typically 1 nm per cycle in case of hexamethyldisilazane (HMDS) gas supply of 50 Pa and HC-O@sub3@ gas supply of 1,000 Pa at 200 ° C. As-deposited film was stoichimetric SiO@sub2@ with no Si-CH@sub3@ bond detected by infrared absorption spectroscopy. Leakage current through the film was satisfactory low, i.e. lower than 10@super -7@ A/cm@super 2@ for 3 MV/cm electric field application. However, a film deposited with a higher deposition rate contained a few wt. % Si-OH bonds and H@sub 2@O molecules. We have already confirmed that a UV-light irradiation to Si substrate through an O@sub 3@ atmosphere serves to enhance the chemical reaction at Si surface because of the generation of an excited state oxygen atom in gas phase as well as the temperature rise of uppermost Si region. We are now investigating that the usage of UV irradiation together is effective for achieving both high quality film formation and high deposition rate.

4:00pm **TF-WeA7 Strontium Oxide Template Monolayers by Surface Reactions of Metal-Organic Precursors with Si(100)***, **A.C. Cuadra**, D. Skliar, B.G. Willis,* University of Delaware

The crystalline structure of strontium titanate (SrTiO@sub3@) consists of alternating 'sublayers' of SrO and TiO@sub 2@. Investigations by molecular beam epitaxy using elemental sources have shown that the heteroepitaxy of SrTiO@sub 3@ on Si(100) 2x1 surfaces can be nucleated with the SrO/Si(100) interface.@footnote 1@ This talk presents the experimental approach for monolayer growth of a SrO 'template' on a Si(100) 2x1 surface using strontium dipivaloylmethanate [Sr(dpm)@sub 2@] and water precursors as the sources of Sr and oxygen, respectively. To nucleate SrO on Si(100), the surface chemistry of the substrate must be tuned to direct the surface reactions of the strontium metal-organic precursor. Following native oxide desorption, dissociative chemisorption of H@sub 2@O is carried out in UHV to hydroxyl terminate Si(100) and initiate two-dimensional nucleation of the metal oxide while avoiding incubation periods common to the atomic layer deposition (ALD) of metal oxides. Metal oxide growth has been correlated to the concentration of hydroxyl groups on the substrate surfaces because they facilitate ligand exchange from the surface.@footnote 2@ Results show that thick SrO films with low carbon contamination can be grown on Si(100) and SiO@sub 2@ terminated with hydroxyl groups through wet chemical methods; this talk focuses on the initial SrO nucleation layer. In situ Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and reflection high energy electron diffraction (RHEED) are used to investigate the crystalline quality of the nucleation monolayers and to verify the epitaxial orientation of SrO films on Si(100) 2x1 surfaces. @FootnoteText@ @footnote 1@ G.Y. Yang, et al., Journal of Material Research, 17 (1), 204-

213 (2002)@footnote 2@ R.L. Puurunen, Applied Surface Science, 245, 6-10 (2005).

4:20pm **TF-WeA8 Texture Evolution during Shadowing Growth of Ru Nanorods***, **F. Tang**[1], T. Karabacak, G. Churamani, G.-C. Wang, T.-M. Lu,* Rensselaer Polytechnic Institute

A detailed study of texture evolution during oblique angle deposition of ruthenium vertical nanorods by dc magnetron sputtering is presented. The Ru nanorods have diameters less than 130 nm and lengths ranging from ~ 40 to ~ 480 nm. We used reflection high energy electron diffraction (RHEED) to characterize texture and demonstrated that RHEED can be a powerful tool to follow the growth front of texture evolution. The diffraction patterns showed that the nanorods developed into a strong vertical (100) texture unlike the usually observed (002) texture of conventional Ru films grown by normal incidence deposition. Furthermore, through the quantitative analysis of the RHEED patterns, it was found that the dispersion angle, @Delta@@theta@, of the texture evolved into a power law relationship with respect to time t before its saturation, @Delta@@theta@ ~ t@super p@, where p = - 0.49 ± 0.01. This is shown for the first time that the power law relationship exists not only in the process of morphology evolution but also texture evolution under oblique angle deposition. The analyses of SEM and TEM images reveal the column competition growth, column dispersion, and the single crystal structure of the individual nanorod. We correlate the evolution of column dispersion angle to the evolution of the texture dispersion angle. We also simulated the evolution of the column dispersion angle based on a modified needle model. The exponent of the power law relationship obtained from the simulation was consistent with experimental value and almost independent of the initial simulation conditions, which may indicate a universal scaling behavior. *F.T. is the recipient of the Harry Meiners Fellowship.

4:40pm **TF-WeA9 Microstructural Characterization of Single Crystal Ferromagnetic Shape Memory Films***, **T.C. Shih**, S. McKernan, S.K. Srivastava, J.Q. Xie, R.D. James, T.W. Shield, C.J. Palmstrom,* University of Minnesota

Microstructure and martensitic phase formation behavior are known to be important for magnetic-field-induced-strain in ferromagnetic shape memory alloys. Transmission electron microscopy (TEM) has been used to examine the microstructure and martensitic transformation behavior of non-stoichiometric Ni-Mn-Ga and Co-Ni-Ga post-growth-released single crystal films grown by molecular beam epitaxy (MBE) on GaAs (001). The twin and precursor tweed structures observed in the TEM images are of particular interests. The film compositions were determined using Rutherford backscattering spectrometry (RBS), particle-induced X-ray emission (PIXE), energy dispersive spectroscopy (EDS), and wavelength dispersive spectroscopy (WDS). For a thin film with nominal composition Co@sub 50@Ni@sub 25@Ga@sub 25@, convergent beam electron diffraction patterns indicated that the austenite exhibited primarily B2 ordering with additional weak L2@sub 1@ ordering at room temperature. Sharp satellite reflections appeared at 1/6 the spacing of the {220} reflections around the {220} spots along the directions at ~250 K, with the evidence of high-density striations or tweed contrast observed in the dark-field images. The tweed contrast became more pronounced on cooling, accompanied by increasing intensity of the four additional reflections. On further cooling and stabilizing at 100 K, no twin structure was observed. For thin films with nominal composition Ni@sub 50@Mn@sub 25@Ga@sub 25@, Ni@sub 50@Mn@sub 30@Ga@sub 20@, and Ni@sub 53@Mn@sub 25@Ga@sub 23@, the martensitic transformation temperatures showed linear dependence with increasing average valence electron concentration per atom (e/a). Each specimen transformed into different microstructures with the microtwins ranging from 10 nm to 80 nm. This presentation will emphasize the influence of composition and epitaxial growth conditions on the resulting microstructure of the FSMA films before and after being released from the substrates.

5:00pm **TF-WeA10 Vinyltrimethylsilane (VTMS) as a Probe of Chemical Reactivity and Surface Structure of a TiCN Diffusion Barrier Deposited on Silicon***, L. Pirolli, **A.V. Teplyakov**,* University of Delaware

This study presents the first molecular level investigation of chemical reactivity of a surface of an amorphous diffusion barrier film deposited on a Si(100)-2x1 single crystal. Vinyltrimethylsilane (VTMS) is chosen as a probe molecule because of its role as a ligand in a common copper deposition precursor, hexafluoroacetylacetonato-copper-vinyltrimethylsilane. Surface chemistry of vinyltrimethylsilane (VTMS) on TiCN-covered Si(100)-2x1 has been investigated using multiple internal reflection Fourier-transform infrared spectroscopy (MIR-FTIR), Auger electron spectroscopy (AES), thermal desorption mass spectrometry, and computational analysis. On a film deposited at 600 K, VTMS adsorbs molecularly at cryogenic temperatures even at submonolayer coverages, the major pathway for its temperature-programmed evolution is desorption. Adsorption at room temperature leads to chemisorption via a double bond attachment. The desorption studies combined with the computational analysis suggest that the adsorption of VTMS occurs preferentially in two configurations: across the surface C-Ti bond and on a corner Ti, but not across the Ti-N bond.

Vacuum Technology
Room 201 - Session VT-WeA

Hydrogen, Outgassing, and Vacuum Systems

Moderator: L. Westerberg, Uppsala University, Sweden

2:00pm **VT-WeA1 System Modeling and Proof of Performance for Large Vacuum Systems***, **J.P. Luby**,* BOC Edwards

Vacuum system modeling is the foundation of vacuum system component selection and provides the user tangible performance prediction. This paper examines vacuum system modeling and vacuum equipment selection for large vacuum systems and introduces the requirements and challenges of proving the performance of a large vacuum system. With rigorous applications engineering, performance modeling and component testing it is possible to provide a detailed performance statement to the user in the early stages of vacuum system design and build.

2:20pm **VT-WeA2 The ISAC Targets Vacuum System***, I. Sekachev,* TRIUMF, Canadian Research Laboratory, Canada*; **D. Yosifov**,* TRIUMF, Canadian Research Laboratory

ISAC (Isotope Separator and ACcelerator) facility at TRIUMF has been in full operation since 1999. The ISAC East and West targets use the proton beam from the cyclotron to produce various radioactive isotope species in the target, which are then ionized and extracted. The ions are then passed through the mass separator and the selected ions are distributed to the low energy experiments or injected into an RFQ accelerator. The accompanying radioactive contamination from the production of radioactive ions requires the vacuum system to be quite complex. The main target vacuum space consists of two semi-separate (primary and secondary) volumes pumped by 1000L/s turbomolecular pumps. The primary volume uses four pumps while the secondary volume uses two pumps. The nominal vacuum in both volumes is about 1.0E-6 Torr. The pressure is monitored by two cold cathode ion gauges and two hot filament ion gauges. Both cold cathode gauges are used to interlock the system during the bake out of the target and beam production. Three exhaust gas storage tanks (decay tanks) are used for handling radioactive gasses and controlled release of the gasses to the atmosphere. The two ALCATEL hermetic rotary vane pumps are used as backing pumps. The gas specie insensitive membrane gauges are used for monitoring the storage tank pressures. This paper describes the details of the ISAC target vacuum system as well as some procedures related to the handling of the radioactive gasses produced by the targets.

2:40pm **VT-WeA3 Pumping Speed Measurement of TiZrV Coated Pipes***, **A. Bonucci**, A. Conte,* SAES Getters S.p.A., Italy

In the last few years the interest of the particle accelerators community towards ZrTiV non evaporable getter (NEG) coatings of vacuum chambers has been continuously increasing. With the increase of the interest, also the number of characterizations of this coating from several final users is increasing. One of the key characterizations is the measure of the actual pumping speed of the NEG coating. The typical method used to measure the pumping speed of a getter is described in the ASTM F798-82. Normally, it has been applied onto a discrete sample coated during the process. This approach is not suitable with NEG coated vacuum pipes. An improved experimental configuration for sorption tests is here first described. The method is based on the ratio measurement of pressures at the inlet and the outlet of a coated pipe. A calibration curve permits to evaluate sticking probability of the coated surface from the pressure ratio. A mono-dimensional model is often used in order to obtain the calibration relationship; for high sticking probability this approach is not more suitable. We will show that a three dimensional mathematical model, based on the angular coefficients approach, is needed to calculate the gas distribution

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[1] **TFD Student Award Winner**

inside a vacuum vessel and the relationship between the pressure ratio and the specific pumping speed of the coated surface.

3:00pm **VT-WeA4 Beam Induced Dynamic Pressure Rise in RHIC*, H. Hseuh,*** *S.Y. Zhang,* Brookhaven National Laboratory

Relativistic Heavy Ion Collider (RHIC) consists of two storage rings of 3.8 km in circumference for high energy and nuclear physics research. With increasing ion beam intensity during recent RHIC operations, rapid pressure rises of several decades were observed at most warm sections and at a few cold (4.5K) sections. The pressure rises are associated with electron multi-pacting, electron stimulated desorption and beam ion induced desorption; and have been one of the major luminosity limiting factors. This dynamic pressure rises will be explained based on the observations at RHIC and the existing understandings. Some remedies to reduce the pressure rises, such as in-situ baking, NEG coating and solenoids, have been implemented over the last few years and their effectiveness will be illustrated. *Work performed under Contract No. DE-AC02-98CH1-886 with the auspices of the US Department of Energy.

3:20pm **VT-WeA5 Hydrogen in Vacuum Systems: An Overview*, R.A. Outlaw,*** College of William and Mary **INVITED**

Ubiquitous hydrogen plays a dominant role as the primary residual gas in low to ultrahigh vacuum, either in the form of water (unbaked systems) and/or in the form of molecular hydrogen (baked systems). Because of the very small size of the atom, hydrogen resides in interstitial sites, point, line, 2d and 3d defects in the bulk of virtually all materials and is the primary source of outgassing. At the vacuum interface, hydrogen is also located in the form of metal hydroxides. The effective outgassing rate for a given vacuum material is a function of the hydrogen surface concentration which, in turn, is a function of the density of the aforementioned sites and defects. System processing significantly affects the magnitude of the hydrogen concentration and can vary by many orders of magnitude. It is, therefore, quite difficult to analytically characterize the molecular dynamics in UHV systems without accurate knowledge of the existing concentration. In this review, the relevant parameters connected with the location and transport of hydrogen (primarily for stainless steel, but also for aluminum and other selected system materials) is presented. Gas phase variations are correlated with the surface complex chemical composition, thickness and concentration of defects. Surface diagnostics, such as AES, XPS, TDS and TOF-SIMS were employed to determine the sources of hydrogen, desorption mechanisms and the magnitude of outgassing into the vacuum space. Hydrogen solubilities and diffusivities are also presented. System processing, such as, thermal bake, glow discharge cleaning, molecular scrubbing and other outgassing reduction methods are compared. The magnitude of hydrogen outgassing is correlated with the extent of system processing.

4:00pm **VT-WeA7 Hydrogen in Vacuum Systems*, B. Hjörvarsson,*** Uppsala University, Sweden **INVITED**

Hydrogen is found as an impurity in all materials. The only relevant question in that context is how much there is and which influence it has. In this contribution I will discuss the possibility of influencing the hydrogen content and diffusion rate in materials. Special emphasis will be on what can be learned from modern thin film growth and how thin film techniques can be used to improve materials design and performance. Examples from magnetism, elasticity and outgassing will be highlighted in this context.

4:40pm **VT-WeA9 Explosive Nature of Hydrogen in a Partial Pressure Vacuum*, T.M. Jones,*** *W.R. Jones,* Solar Atmospheres Inc.

The explosive nature of hydrogen is well reported at atmospheric conditions. However, the explosive properties of hydrogen in a sub-atmospheric pressure are not well known. Hydrogen has desirable characteristics for many processes but using hydrogen in an atmosphere that is primed for an explosion must have several safeguards and an understanding of its explosive limits, vacuum or otherwise. A laboratory vessel was constructed to withstand hydrogen explosions to test these principals. Topics of discussion will include mixtures of hydrogen and air in partial pressure vacuum, and determination of the explosive ranges. Sources of ignition will be discussed and how the ignition source and location can affect the explosive characteristics. Other topics of discussion will be what types of safeguards could be used, more specifically an oxygen probe, and how these safeguards can be employed to prevent a catastrophic explosion.

5:00pm **VT-WeA10 Low Outgassing of Silicon-Based Coatings on Stainless Steel Surfaces for Vacuum Applications*, D.A. Smith,*** *M.E. Higgins,* Restek Corporation*; B.R.F. Kendall,* Elvac Associates

Comparative tests of stainless steel vacuum chambers and components with and without silicon-based passivation coatings showed exceedingly low rates of gas evolution from the coated surfaces. A variety of approaches have been used to illustrate the low outgassing qualities of vacuum systems and vacuum components modified with an amorphous silicon deposition layer. For example, the samples are heated and cooled in turn while the outgassing rates are recorded at temperatures up to 250 degrees C. Base pressures ranged from 10-7 Torr to 2.5 x 10-10 Torr. In other experimentation, the outgassing characteristics of systems in the 10-5 to 10-7 Torr vacuum range are compared. The coatings are resilient, inert and capable of withstanding temperatures above 400 degrees C. As well as their obvious potential for reducing outgassing rates in vacuum chambers thereby allowing shorter pump-down times with smaller vacuum pump systems, they have proved useful in minimizing errors due to thermal desorption in experimental metal-envelope ionization gauges operating down to the low 10-10 Torr range.

Applied Surface Science
Room 206 - Session AS+TF-ThM

Thin Film Characterization

Moderator: P.M.A. Sherwood, Oklahoma State University

8:20am **AS+TF-ThM1 Characterization of Nanoscale Ceramic Gradient Coatings for Gas Analytical Microdevices***, **M. Bruns**, V. Trouillet, H. Mueller, E. Nold,* Forschungszentrum Karlsruhe GmbH, Germany*; R.G. White,* Thermo Electron Corporation, England

The key element of the Karlsruhe Micro Nose is a thumbnail sized gas-sensitive microarray which at present consists of 38 sensor elements on an area of 4x8mm@super 2@. It is based on a noble metal-doped SnO@sub 2@ layer, the electrical conductivity of which is highly sensitive to the composition of the ambient atmosphere and is measured between adjacent parallel platinum strip electrodes. In order to enable pattern recognition techniques these initially identical sensors have to be gradually differentiated with respect to their gas response. For this purpose gas-permeable membranes with thickness variation of approximately 2 to 10 nm were deposited across microarray using ion beam assisted deposition. In this work we focus on mixed membranes combining the gas permeability of silica and the chromatographic discriminating capability of alumina. Different geometries were achieved by shaping the ion beam profile to gradually alter the ion current density across the microarray leading to laterally different deposition rates. Various Al/Si ratios within the membranes were obtained using different substrate temperatures during deposition. In the present paper a comprehensive characterization of differently shaped nanoscale membranes is reported. Auger electron spectroscopy is used for evaluation of the geometrical integrity of the uncoated electrode pattern and for the determination of thickness profiles, respectively. Parallel angle resolved X-ray photoelectron spectroscopy provides thickness information for the membranes together with information on chemical binding states in a non-destructive manner. Ellipsometry is presented as a powerful quantification method for the determination of the desired ultra thin membrane thickness profiles. Moreover, after calibration with surface analytical data, ellipsometry allows for rapid evaluation of Al/Si concentrations ratios within the membranes.

8:40am **AS+TF-ThM2 Characterization of Low k Dielectrics Using Auger Microprobe Analysis***, **C. Dziobkowski**,* IBM Corporation, E. Fishkill*; E.D. Adams,* IBM Corporation, Essex Jct.*; J.A. Coffin, R.E. Davis, P.L. Flaitz,* IBM Corporation, Hopewell Jct.*; E.G. Liniger,* IBM Research, Yorktown Heights*; S.E. Molis, D.D. Restaino,* IBM Corporation, Hopewell Jct.

As the dimensions of integrated circuits are reduced, the capacitance between metal lines has an ever increasing impact on device performance. It increases circuit delay, results in parasitic capacitance creating crosstalk, degrades the signal to noise ratio and increases power consumption. Reduction of capacitance by employing low k dielectric materials is thought to be a solution. These low k materials have to be characterized as to their composition, uniformity, void formation and oxygen permeability requirements. This paper gives a description of the methodology developed using Auger depth profile analysis to characterize these new materials. Also important is how these Auger microprobe results can be compared to data obtained from TEM, TOF-SIMS and Rutherford backscattering analyses. The synergism of these analytical techniques is necessary to obtain the understanding needed for the integration of these low k dielectric materials with copper metallurgy in successful device fabrication.

9:00am **AS+TF-ThM3 Semiconductor-Dielectric Interfaces: Composition and Structure***, **L.C. Feldman**, S. Dhar,* Vanderbilt University*; J.R. Williams,* Auburn University*; L. Porter,* Carnegie- Mellon University*; J. Bentley,* Oak Ridge National Laboratory*; K.-C. Chang, Y. Cao,* Carnegie-Mellon University **INVITED**

The semiconductor-dielectric interface is the key to a successful MOSFET technology and has played the essential role in the silicon revolution. Wide-band gap materials have presented a challenge to achieve the same degree of interface perfection as silicon, although considerable progress is underway. The SiC/SiO2 interface is of particular scientific interest in this development because of its close relationship to silicon, both in processing and structure. The oxidation process in SiC yields a heavily defected SiC/SiO2 interface giving rise to poor device characteristics. Systematic use of chemical modification and processing, combined with a careful analysis of interfacial structure, results in significant progress in reducing defects and increasing inversion layer carrier density and mobility. For example nitridation of this interface results in a remarkable improvement and is a driving force for understanding the nitrogen profile and concentration. The quantitative nitrogen profile is critical to this understanding and provides a significant depth profiling challenge. Using a variety of probes including medium energy ion scattering, secondary ion mass spectroscopy, nuclear profiling and electron energy loss spectroscopy we show that the nitrogen is confined to within ~1.5 nm of the buried interface, with concentrations that are crystal face dependent and vary from 0.5 to ~1.5 x 10@super 15@/cm@super 2@. From an analysis point of view the significant new finding is the comparison of techniques and the degree of quantitative agreement between the different probes. @FootnoteText@ Supported by DARPA, N00014-02-1-0628 and ONR,N00014-01-1-0616. Research at the O. R. N. L. was sponsored by the Division of Materials Sciences and Engineering, U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

9:40am **AS+TF-ThM5 Comparison of Silicon Oxynitride Produced by PIII/D and Reactive Sputtering***, **N.D. Theodore**, M. Bagge-Hansen, B.C. Holloway, D.M. Manos,* College of William and Mary*; C. Hernandez, T. Siggins, H.F. Dylla,* Jefferson Lab

High-purity, hydrogen-free silicon oxynitride films were successfully created using two techniques, plasma immersion ion implantation/deposition (PIII/D) and reactive sputtering. Our previous work has shown that coating 6" polished 304 stainless steel electrodes with silicon oxynitride, created by PIII/D, dramatically reduces field emission from 27 µA of at 15 MV/m to 160 pA at 30 MV/m. We have recently developed a new procedure to deposit silicon oxynitride without ion implantation using a low temperature (<200°C) Rf reactive sputtering process. Both procedures use a 750 W inductively-coupled nitrogen plasma that sputters silicon dioxide from a quartz dielectric window. The purpose of this study was to determine and compare the composition and electrical properties of the silicon oxynitride coatings created using the reactive sputtering and PIII/D procedures. The homogeneity, stoichiometry, and density of deposited/implanted layers were determined using Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FTIR), and Rutherford backscattering spectrometry (RBS). AES depth profiles determined that both procedures created homogeneous films, and FTIR and XPS spectra confirmed the creation of silicon oxynitrides with approximately 10% nitrogen. Ultraviolet photoelectron spectra and capacitance-voltage measurements will also be presented and discussed.

10:00am **AS+TF-ThM6 Microbridge Testing of Plasma Enhanced Chemical Vapor Deposited Silicon Oxide Films on Silicon Wafers***, **Z. Cao**,* Boston University*; T.-Y. Zhang,* Hong Kong University of Science and Technology*; X. Zhang,* Boston University

Plasma-enhanced chemical vapor deposited (PECVD) silane-based oxides (SiOx) have been widely used in both microelectronics and MEMS (MicroElectroMechanical Systems) to form electrical and/or mechanical components. During fabrication of such microelectronic and MEMS devices, PECVD SiOx undergo many thermal cycles, which often causes unwanted changes in thermal-mechanical properties of the material, and consequent degradation of device performance and reliability. In this paper, a novel nanoindentation-based microbridge testing method for thin films is proposed to measure both the residual stresses and Young's modulus of PECVD SiOx thin films. In this method, freestanding microbridges are fabricated from the thin films using the micromachining techniques. The tests are performed at the center of the microbridges with an instrumented nanoindentation system and the load-deflection curves are recorded. Our theoretical model used a closed formula of deflection vs. load, considering both substrate deformation and residual stress in the thin film. To simulate real thermal processing in device fabrication, some microbridges underwent various rapid thermal annealing (RTA) at temperatures up to 800ÂºC. An interferometric microscope was also used to measure the curvature profiles of the bridges. Together with nanoindentation test results on the microbridges, we were able to decide the changes in residual stresses and Youngâ?Ts modulus of the PECVD SiOx thin films under different thermal annealing. Two factors, density change and plastic deformation, were identified as controlling mechanisms of stress changes in the films. A microstructure based mechanism elucidates "seams" as source of density change and "voids" as source of plastic deformation, accompanied by viscous flow. This mechanism was applied to explain our experimental results of thermal annealing of PECVD SiOx films.

10:20am **AS+TF-ThM7 Characterization of Ultra Shallow Arsenic Implants by ARXPS, LEXES, MEIS, and Dynamic SIMS***, **G. Conti**, Y. Uritsky, H. Graoui, M. Foad,* Applied Materials*; C.R. Brundle,* Brundle & Associates*; D. Kouzminov,* Materials Analytical Services*; C. Hitzman,* Full Wafer Analysis*; P. Mack, J. Wolstenholme,* Thermo Electron Inc., UK

Ultra-shallow As implants are a leading-edge technology. Low voltage results in implant layers of tens of A thickness after anneal. Reliable metrology for shallow implants is needed. We characterize the implant layer as a function of nominal dose (1E14 to 2E15 ions/cm2) at 2KV, using a variety of techniques. Angle Resolved-XPS gives precise measurement of SiO2 oxide thickness, monitors the chemical state of As, and gives a non-destructive rough depth profile. Low Energy X-Ray Emission Spectroscopy, LEXES, gives a non-destructive As dose measurement, which depends on calibration against a bulk standard, for accuracy. MEIS gives a non-destructive depth distribution of atoms not in Si substitutional sites, and a dose calibrated by reference to amorphised Si. Dynamic SIMS provides very precise dose and depth distribution measurement to very low As concentrations, but is destructive and has a problem with the initial part of the depth scale and any As dose within it. Taken together a complete picture of the implant layer is obtained. Prior to annealing the As has a broad distribution, centered at about 50A depth. The outer oxide layer increases from 13A at 1E14 ions/cm2 dose to 18A for 2E15 ions/cm2 dose. ARXPS showed that samples from one particular implanter had a component of As2O3 very near the surface, well removed from the elemental As implant. The annealing conditions (N2 with 10% O2) double the oxide thickness (22A at 1E14 ions/cm2 dose; 38A at 2E15 ions/cm2), and cause the As to pile up just on the Si side of the SiO2/Si interface, but with a strong diffusion tail to 150A depth (SIMS). XPS shows that any oxide component is eliminated by anneal. A comparison of the MEIS to the SIMS depth distributions shows that the diffusion tail is in substitutional sites, and therefore not observable in the MEIS.

10:40am **AS+TF-ThM8 Hot Electron Transport Across Manganese Silicide Layers on the Si(001) Surface***, **A. Stollenwerk**, M.R. Krause, V.P. LaBella,* University at Albany SUNY

The need for high efficiency spin injection for spintronic applications has led to the study of different ferromagnetic interfaces. Recent theoretical studies have shown that the MnSi interface orders ferromagnetically.@footnote 1@ We performed ballistic electron emission microscopy (BEEM) on the MnSi/Si(001) Schottky barrier to study the hot electron transport properties. BEEM allows the interface to be probed on the nanometer scale and also gives the option to perform spin dependent measurements. Samples for this study were fabricated by electron beam deposition of Mn onto n-type Si(001) with thicknesses ranging from 50 to 200 Å. These layers were annealed at various temperatures in ultra high vacuum (UHV). The front side contact was fixed ex situ before the sample was reinserted into UHV to perform BEEM. Film composition has been determined by secondary ion mass spectroscopy (SIMS). The Schottky heights have been determined by fitting the BEEM spectra to the Bell-Kaiser model. The effects of temperature, film thickness and composition on the BEEM current will be discussed. @FootnoteText@ @footnote 1@S.A. Wolf et al., Science 294, 1488 (2001).

11:00am **AS+TF-ThM9 Optimization and Deposition of CdS Thin Films As Applicable to TiO@sub2@/CdS Composite Catalysis***, **K. Prabakar**, T. Takahashi,* Toyama University, Japan*; T. Nakashima,* Kashiwa Chuo High School, Japan*; Y. Kubota,* Yokohama City University, Japan*; A. Fujishima,* Kanagawa Academy of Science and Technology, Japan

Recently, the study of interparticle electron transfer between dissimilar semiconductors has received interesting investigations. Combining two semiconductor particles offers an opportunity to sensitize a semiconductor material having a large bandgap and energetically low-lying conduction band by another one having a small band gap and energetically high-lying conduction band. In our investigations, photosensitization of TiO@sub2@ by narrow band gap semiconductor such as CdS have been investigated and found to be effective for separation and transfer of photoexcited charge carriers. The TiO@sub2@ thin films were deposited by direct current reactive magnetron sputtering and CdS by chemical bath deposition. Thin films of CdS were deposited from a solution of analytical grade CdSO@sub4@ (1 M) and thiourea (1 M) in an alkaline solution of ammonia with a total volume of 80 ml. The temperature and time of the deposition were varied between 65 to 80 ° C and 30 to 60 minutes respectively. To vary the composition of the films, different concentrations of CdSO@sub4@ and thiourea were used. The optical band gap energy varied from 2.41 to 2.59 eV as the CdSO@sub4@ solution concentration increased from 0.4 to 2.8 ml while keeping the thiorea as 1.6 ml. The as deposited films were annealed at different temperatures to study the effect of structural (XRD) and surface properties (SEM and AFM) on the efficiency of the TiO@sub2@/CdS catalysis. The TiO@sub2@ films were found to be polycrystalline anatase structure with optical band gap energy of 3.1 eV. The degradation efficiency under visible light of methanol and methylene blue by TiO@sub2@/CdS films were investigated by FTIR and spectrophotometer respectively and the results are discussed in details. The visible light photocatalytic degradation efficiency TiO@sub2@/CdS is far higher than that of TiO@sub2@ film.

Biomaterial Interfaces
Room 311 - Session BI1-ThM
BioMEMS and Microfluidics

Moderator: G.P. Lopez, University of New Mexico

8:20am **BI1-ThM1 Long Lifetime Polymer Microfluidic Devices for HPLC-MS Applications***, **K.L. Seaward**, D.L. Ritchey, K.P. Killeen, H. Yin, R.A. Brennen,* Agilent Laboratories

Polymer microfluidic devices have been developed for High Performance Liquid Chromatography with integrated nano-electrospray tips for interfacing to Mass Spectrometry. HPLC-MS is regarded as a preferred analytical technique for protein identification in very small (nanoliter) volumes of sample and has been used, for example, to determine protein content in blood. Commercially available microfluidic devices consist of separate parts for liquid chromatography and electrospray functionality connected with fittings. This leads to difficulties in use, compromised performance, and complicated fabrication. The devices described in this presentation are made in a biocompatible polyimide and contain sample enrichment and liquid chromatography columns plus electrospray tips. Their size is approximately 2.5cm x 6cm with 200-400 micron thickness in a multi-layered structure made by direct laser writing of patterns followed by vacuum lamination. Laser cutting of electrospray tips and incorporation of metal traces in the layer structure provide electrospray functionality. A rotary valve interface between high-pressure fluids delivered by a nanoflow pump and the microfluidic device itself provides efficient fluid switching between various ports on the device. Gas-phase plasma processes, similar to those found in microelectronic device manufacturing, are used in the fabrication process. These are critical to ensure long lifetime performance of the devices, resulting in repeatable high-pressure performance of the column structures and stable electrospray behavior. In combination with mass spectrometry, state-of-the-art attomole level detection of protein digests has been demonstrated using these microfluidic devices. The device fabrication will be outlined and recent applications to proteomics will be shown.

8:40am **BI1-ThM2 BioMEMS Chip and Package Design for Surface-Controlled Bioreaction Processes***, **J.J. Park**, M.A. Powers, X. Luo, R. Ghodssi, G.W. Rubloff,* University of Maryland

BioMEMS research exploiting multi-step, multi-site biomolecular reactions for metabolic engineering and other applications requires an integrated chip, packaging, and control system designs to accommodate fluidic, electrical, and optical networks. We have developed approaches for sealing and re-opening bioMEMS systems to allow reuse and post-process analysis. Photoimageable SU-8 is used on pyrex wafers to create microfluidic channels as micro-knife-edges for sealing to flexible PDMS gaskets. Electrical networks provide Au and ITO electrodes for selective assembly and functionalization of amine-rich chitosan as the platform for biomolecular reaction steps, while integrated SU-8 waveguides enable fluorescence sensing at these sites. PDMS is spun onto a Plexiglas top wafer, inverted, and placed onto the SU-8 channels. The two wafers are then compressed by bolting together a Plexiglas package comprised of top and bottom plates, along with a Plexiglas ring which carries the inputs and outputs to external control systems. The design enables optical microscopy observations from above, which confirm leak-free sealing when colored dye is transported through the microfluidic network. Chitosan polysaccharide, positively charged in low pH solution, is electrodeposited at negative electrodes in the bioMEMS system. This provides a promising avenue for extending to bioMEMS environments our prior work using patterned electrodes on chips in solution, which included selective conjugation of proteins and nucleic acids, as well as enzymatic conversion of small molecules.

9:00am **BI1-ThM3 Artificial Extracellular Matrices: Polymer Films Modified with Positive Cues to Promote Cell Adhesion and Neurite Extension***, **G.T.R. Palmore**, H.-K. Song, D. Hoffman-Kim,* Brown University **INVITED**

Nerve growth is modulated in vivo by positive (permissive or growth-promoting) and negative (growth-inhibitory) biochemical cues. Neurons of the peripheral nervous system (PNS) are able to regenerate after injury because of the endogenous growth-promoting environment provided by Schwann cells. Traumatic injury to the central nervous system (CNS), however, often results in irreversible loss of function because the neurons in the CNS reside in an environment that contains too many negative cues and too few positive cues. We seek to calibrate the quantity of positive cues relative to negative cues needed for CNS regeneration and thus have fabricated patterned substrates of specific dimensions for this purpose. These substrates consist of a conductive polymer matrix doped and chemically modified with biologically-active molecules in varying spatial relationships. The preparation of these substrates will be discussed, including their spectroscopic, microscopic and immunochemical characterization. In addition, results will be shown that demonstrate how these substrates promote cell adhesion and guide neurite extension of neurons in the presence of both positive and negative cues.

9:40am **BI1-ThM5 Study of Molecular Transport in Nanofluidic Channels by Integrated Multiple Internal Reflection Infrared Waveguide***, **T.C. Gamble**, Y.J. Oh, C.H. Chung, D.R. Petsev, S.R.J. Brueck, G.P. Lopez,* University of New Mexico*; C.F. Ivory,* Washington State University*; S.M. Han,* University of New Mexico

We have successfully integrated nanofluidic channels into Si multiple-internal-reflection (MIR) infrared waveguides for the purpose of biomolecular separation and detection. Biomolecules, electrolyte solution, and their reactions can be probed by the MIR waveguide, provided that the channel width is substantially less than the IR wavelength. In the regime where the channel width (10 to 100 nm) is comparable to the Debye length (~20 nm) of the electrolyte solution, we have investigated the electrokinetic transport of fluorescent dyes in a range of pH with the application of transverse "gate" bias in the field effect transistor (FET) configuration.* The gate bias controls the zeta potential and therefore the electroosmotic flow of dye molecules with a possibility of reversing its flow direction. Fluorescent dyes are chosen for the purpose of initial transport studies and visualization. We will also present the effect of ionic strength on the electrokinetic transport of fluorescent dye molecules. The addition of salt increases the ionic strength, but it also adds mobile ions that can move through the thermal SiO@sub 2@ layer that insulates the Si substrate from the electrolyte solution. We evaluate the use of a Si@sub 3@N@sub 4@ sub-layer as a means of preventing the leakage current due to mobile ions moving through the SiO@sub 2@. We compare our observations with fluorescence spectroscopy and current measurements. * U.S. Patent Application was filed on July 19, 2004.

10:00am **BI1-ThM6 Electrochemical Programming of Bioactive Surfaces***, **B.C. Bunker**, M. Farrow, K.R. Zavadil, W.G. Yelton,* Sandia National Laboratories

Self-assembled monolayers containing cyclodextrin have been used as a template for the reversible electrochemical patterning of surfaces. Electrochemical patterning occurs as a result of the oxidation and reduction of functionalized ferrocene in solution. When Fe(II) is present in the ferrocene, this neutral aromatic species is adsorbed by the cyclodextrin surface. When Fe(II) is oxidized to Fe(III), the ferrocene desorbs from the cyclodextrin. The electrochemically switchable surface is of interest in microfluidic systems when the ferrocene is functionalized to interact with specific biological species. We have succeeded in attaching biotin to the ferrocene via an ethylene glycol linkage. The biotinylated ferrocene can be made to adsorb and desorb from cyclodextrin deposited on gold electrodes. We have demonstrated that the biotin on the ferrocene is active toward the adsorption of streptavidin. With programmable streptavidin surfaces, we can create patterns with a wide range of biological species (i.e. any species that can be biotinylated). The synthesis, characterization, and electrochemical switching of the films are described, involving techniques such as cyclic voltammetry, electrochemical stripping, secondary ion mass spectroscopy, ellipsometry, and the quartz crystal microbalance. Use of the switchable films for creating programmable patterns of antibodies in sensors is described.

Biomaterial Interfaces
Room 311a - Session BI2-ThM
Sugars at Surfaces

Moderator: G.P. Lopez, University of New Mexico

10:20am **BI2-ThM7 Chemical Glycomics: Carbohydrates on Surfaces to Screen Biopolymer Interactions***, **P.H. Seeberger**,* ETH Zurich, Switzerland **INVITED**

The growing field of glycomics is suffering from the lack of molecular tools for screening, imaging, purification and other procedures that are routine in studies involving peptides and oligonucleotides. Using an automated oligosaccharide synthesizer we developed some time ago, access to defined oligosaccharides has become very rapid. These synthetic molecules, as well as any isolated carbohydrate, can now be readily converted into a series of tools that aid biological and medical investigations. Described are: 1) Carbohydrate microarrays that require small quantities of material, are fully amenable to HTS technologies to screen carbohydrate interactions with proteins, DNA, and carbohydrates as well as cells; 2) Affinity colums, magnetic beads and carbohydrates containing biotin are used to isolate proteins interacting with oligosaccharides and glycoconjugates; 3) Carbohydrates equiped with fluorescent tags or quantum dots is used to image carbohydrates in vitro and in vivo. Application of these tools to biological problems of medical significance will be discussed. Particular emphasis will be placed on novel aminoglycoside antibiotics, HIV glycobiology and the development of fully synthetic carbohydrate vaccines.

11:00am **BI2-ThM9 Synthetic Glycopolymers as Scaffolds to Study Multivalent Carbohydrate Interaction at Surfaces***, **G. Coullerez**, K. Barth, M. Textor,* Laboratory for Surface Science and Technology, Switzerland

Carbohydrates are information-rich molecules vital in intercellular interactions. As cell surface receptors, they play a role as recognition site for interactions with other cells, viruses or bacteria. To investigate those bio-interactions sugar tools based on carbohydrate chemistry and sensitive analytical techniques are needed. Functionalized surfaces with synthetic carbohydrate-tagged polymers that display multiple copies of the binding sugar units are attractive approaches to mimic interaction at cell-surfaces. They are often multivalent providing strength and specificity. In this aim, we have developed PEG-graft polycationic copolymers tagged saccharides. While spontaneously adsorbed on negatively charged surfaces the copolymers show specific lectin and bacteria recognition. Combined with a photolithography patterning method on metal oxide surfaces (Nb@sub 2@O@sub 5@, TiO@sub 2@), the high specificity of this platform in a non-fouling background is also demonstrated. The glycopolymers can also be synthesized with atom transfer radical polymerization (ATRP) of glycosylated monomers, featuring a wide range of functionalities, molecular weight and polydispersity for specific protein or cell-targeting applications. To demonstrate the versatility of our approaches, we use in particular the well-known mannose-lectin Concanavalin A (ConA) or bacteria E. Coli specific interactions. To sense in situ/in real time and quantitatively the interfacial processes between carbohydrate-modified surfaces and proteins in solution, fluorescence microscopy and optical evanescent field based sensor are used. The carbohydrate surface density is also quantitatively investigated by chemical surface analysis methods (XPS, ToF-SIMS). First applications and case studies using synthetic glycopolymers tagged with mono- or oligosaccharide will be discussed mainly in the context carbohydrate chips for proteins and pathogens detection and delivery vectors to target specific cell receptors.

Electronic Materials and Processing
Room 309 - Session EM1-ThM
Molecular Electronics

Moderator: D.B. Janes, Purdue University

8:20am **EM1-ThM1 Molecular Conductance and Contact Resistance Measured in Nanoparticle-Bridged Nanogap Structures***, **C. Chu**, G.N. Parsons,* North Carolina State University

Understanding molecular conduction and contact resistance at organic-metal junctions is crucial for advanced organic electronic materials and devices. We have developed an angled metal evaporation technique to form planar metal (Au and Al) electrodes with separation distances of <50nm and electrode width of several microns, and used 80nm Au nanoparticles to form conductance pathways between the nanometer-spaced electrodes. Multiple nanoparticles can be measured in parallel, and the conductance increases with the number of nanoparticles in the gap. Before Au nanoparticle deposition, various molecular monolayers were adsorbed onto the Au electrodes, resulting in bridging structures that enable conductance of sets of molecules to be characterized. The conductance and contact resistances are evaluated from current-voltage characteristics and compared to results obtained by conductive probe AFM (CP-AFM) on the same monolayers. Molecules studied include various length alkanethiols and alkylamines, as well as conjugated molecules including xylyl thiol and phenylene derivatives. Current vs voltage is observed to follow the coherent tunneling model, and contact resistance (R@sub o@) was evaluated by measuring the effect of alkyl chain length for both thiol and amine head groups. Alkanethiols show R@sub o@ of ~18 k@OMEGA@, whereas amine head groups give R@sub o@ ~1k@OMEGA@. The number of molecules probed is not precisely known, but resistance for the nanoparticle bridge is larger than measured by CP-AFM, suggesting a smaller number of molecules are probed in the bridge structure. Furthermore conjugated molecules show conductivity that is ~400 times larger than for alkanedithiols. Results show that the bridged nano-gap structure can be used to evaluate conductance and resistance on the molecular scale, and it is capable of characterizing a variety of molecular and nanostructured elements.

8:40am **EM1-ThM2 The Effects of Molecular Environments on the Electrical Switching with Memory of Nitro Molecules***, **N. Gergel-Hackett**,* University of Virginia, US*; N. Majumdar, Z. Martin, G. Pattanaik,* University of Virginia*; Y. Yao, J.M. Tour,* Rice University*; G. Zangari, N. Swami, L.R. Harriott, J.C Bean,* University of Virginia

Since memory behavior was first reported for the "nitro" molecule (an OPE molecule with nitro side groups),@footnote 1@ other researchers have reported various combinations of electrical switching, memory, and/or negative differential resistance.@footnote 2,3,4@ These reports employed test structures that differed in the number of nitro molecules simultaneously contacted: some reports describe devices that contact thousands of molecules,@footnote1,3@ while others contact just a few.@footnote 2,4@ To address a possible correlation between contacting a large area of nitro molecules and observing memory behavior, we report on experiments that use a nanowell device where nitro molecules are seperated by insertion into a secondary matrix of alkanethiols. We observe memory behavior for "pure" nitro monolayers, but not for the monolayers of nitro molecules inserted into alkanethiols. Additionally, insertion into alkanethiol matrices adds the variable of order. STM images reveal that alkanethiol matrices are ordered, yet "pure" nitro monolayers are disordered. A recent report suggests a correlation between the rate of electrical switching and the ordering of a nitro molecule's environment.@footnote 4@ To test for a relationship between memory behavior and an ordered matrix environment, we have developed ways of forming disordered matrices. This is done by changing the exposure time of the substrate to the alkanethiol solution or by using COOH-terminated alkanethiols (16-mercapto hexadecanoic acid). We will report the electrical behavior of nitro molecules inserted into these disordered alkanethiol matrices and contrast the results with those obtained for nitro molecules inserted into ordered matrices, as well as those for "pure" nitro monolayers. @FootnoteText@ @footnote 1@M.A. Reed et al, Appl. Phys. Lett. 78, 3735 (2001)@footnote 2@I. Kratochvilova et al, J. Mater. Chem. 12, 2927 (2002)@footnote 3@F.Fan et al, J. Am. Chem. Soc.124, 5550 (2002)@footnote 4@Z.J. Donhauser et al, Science 292, 2303 (2001).

9:00am **EM1-ThM3 Electronic Structure and Charge Addition Effects in Phenylene Ethynylene Oligomers: a Comparison of Pristine versus -NO@sub2@ Substituted Molecules***, **S.W. Robey**, C.D. Zangmeister, R.D. van Zee,* NIST

Interest in aromatic systems based on phenylene ethynylene oligomers (OPE) has been spurred by reports of intriguing transport behavior in metal-molecule-metal junctions. There have been reports of the observation of negative differential resistance (NDR) characteristics by substitution of electron-withdrawing -NO@sub2@ groups on the central ring of a three-ring phenylene ethynylene oligomer, whereas this behavior is not observed for the "pristine", unsubstituted molecule. In this contribution, the relevant @pi@ electronic structure near the Fermi level, determined via photoelectron spectroscopy for self-assembled monolayers on gold, is compared and contrasted for three-ring phenylene ethynylene oligomers with and without substitution of -NO@sub2@ groups. Further comparison with -NH@sub2@ substituted oligomers and results of ab inito calculations will also be discussed. In addition, theoretical work has invoked redox-like or polaronic effects to provide an explanation for NDR behavior. We have performed measurements to shed light on this issue by comparison of the influence of additional charge in pristine versus nitro-substituted OPE, added by "doping" with K. For pristine OPE, sequential addition of K leads to a gradual shift of levels to higher binding energy reminiscent of "rigid band" behavior, although some distortion/conformation change is suggested by relative shifts of @pi@ levels. For large charge addition, two new states are observed in the original @pi@ to @pi@* gap. For the nitro-substituted oligomer, a similar spectrum is observed for large K addition, but the behavior as a function charge addition is quite different. After an initial shift by ~ 0.6 eV, the spectrum is nearly pinned for subsequent K addition before a final shift brings it to near coincidence with the pristine oligomer spectrum. These results will be discussed in the context of polaronic/bipolaronic effects and the influence of unoccupied levels related to the -NO@sub2@ substitution.

9:20am **EM1-ThM4 Probing Silicon Based Molecular Electronics with Ultra-High Vacuum Scanning Tunneling Microscopy***, **N.P. Guisinger**, N.L. Yoder, M.C. Hersam,* Northwestern University

A cryogenic variable temperature ultra-high vacuum (UHV) scanning tunneling microscope (STM) is utilized for measuring the electrical properties of isolated cyclopentene molecules adsorbed to the degenerately p-type Si(100)-2x1 surface at a temperature of 80 K. Current-voltage curves taken under these conditions show negative differential resistance (NDR) at positive sample bias in agreement with previous observations at room temperature.@footnote 1-3@ The enhanced stability of the STM at cryogenic temperatures was utilized for repeated measurements taken over the same molecule. Current-voltage curves on isolated cyclopentene molecules are demonstrated to be repeatable and possess negligible hysteresis for a given tip-molecule distance. Subsequent measurements with variable tip position show that the NDR voltage increases with increasing tip-molecule distance. Using a one-dimensional capacitive equivalent circuit and a resonant tunneling model, this behavior can be quantitatively explained, thus providing insight into the electrostatic potential distribution across a semiconductor-molecule-vacuum-metal tunnel junction. This model also provides a quantitative estimate for the alignment of the highest occupied molecular orbital (HOMO) of cyclopentene with respect to the Fermi level of the silicon substrate, thus suggesting that this experimental approach can be used for performing chemical spectroscopy at the single molecule level on semiconductor surfaces. Overall, these results serve as the basis for a series of design rules that can be applied to silicon-based molecular electronic devices. @FootnoteText@ @footnote 1@ Guisinger, N. P., Basu, R., Baluch, A. S. & Hersam, M. C. (2003) Ann. N. Y. Acad. Sci. 1006, 227-234.@footnote 2@ Guisinger, N. P., Greene, M. E., Basu, R., Baluch, A. S. & Hersam, M. C. (2004) Nano Lett. 4, 55-59.@footnote 3@ Guisinger, N. P., Basu, R., Greene, M. E., Baluch, A. S. & Hersam, M. C. (2004) Nanotechnology 15, S452-S458.

9:40am **EM1-ThM5 Metal Molecule Silicon Devices***, **A. Scott**, D.B. Janes,* Purdue University

While the majority of molecular electronic devices have employed metal contacts, semiconductor contacts could allow more stable chemical bonds and enhanced electrical functionality. Integrating molecular devices on silicon is a promising approach to molecular electronics@footnote 1@ and would leverage capabilities of the microelectronics industry. In this study, metal-molecule-silicon devices have been fabricated and characterized. Molecules are grafted to 111 silicon surfaces by electrochemical reduction of diazonium salts,@footnote 2@ resulting in robust molecular layers that are covalently bound to the surface by C-Si bonds. Aromatic molecules with various headgroups have been grafted to Si and characterized using infrared spectroscopy and cyclic voltammetry. Metal top contacts are deposited using an indirect evaporation technique which minimizes metal penetration, as demonstrated previously on GaAs.@footnote 3@ Electrical testing of these devices indicates that transport can be modulated by both substrate doping and molecular chemistry. If a large metal-semiconductor barrier is present and the substrate is lightly doped, the current-voltage characteristics are only slightly modified by the addition of a molecular layer. N-type Si-Au Schottky diodes (N@sub D@=10@super 15@cm@super -3@) have current densities of 3 A/cm@super 2@ at 0.5 volt, and the addition of a molecular layer reduces the current density by less than an order of magnitude. In devices where the barrier height is small and the substrate heavily doped, transport is more dominated by molecular effects. P+ (N@sub A@=10@super 19@cm@super -3@) Si-Au Schottky diodes exhibit current densities of 10@super 6@ A/cm@super 2@, and the addition of a molecular layer decreases this by 1 to 4 orders of magnitude depending on the molecular species. @FootnoteText@ @footnote

1@Guisinger et al., Nano Let. 55-59, 2004@footnote 2@Allongue et al.,JEAC 161-174, 2003@footnote 3@Lodha and Janes, APL, 2809-2811, 2004.

10:00am **EM1-ThM6 Chemically Resolved Electrical Measurements within Monomolecular Layers*, H. Cohen,* ***R. Yerushalmi, N. Granit, A. Shukla, M.E. van der Boom, A. Scherz,* Weizmann, Israel

Interesting electrical characteristics within monomolecular layers are revealed by chemically resolved electrical measurements (CREM).@footnote 1,2@ The method is based on slightly modified X-ray photoelectron spectroscopy (XPS), using energy-filtered electrons as fine and flexible electrodes. Our recent results manifest breakthrough capabilities for future molecular electronics applications. @FootnoteText@ @footnote 1@ H.Cohen, Applied Physics Letters 85, 1271 (2004).@footnote 2@ H. Cohen, C. Nogues, I. Zon and I. Lubomirsky, J. Appl. Phys., in press.

10:20am **EM1-ThM7 Conduction through Cytochrome c Molecules*, T. Matsumoto,*** *M. Kataoka, T. Kawai,* Osaka University, Japan

Cytochrome c, which mediates electron transfer in biological system, is a candidate molecule with the suitable structure for electronic elements that comprise insulating and active parts. Since this redox center is isolated from the surroundings by the insulating part, the structure of cytochrome c can be regarded as a double tunneling junction for single electron tunneling. However, thin film of cytochrome c shows low conductivity, whereas, in vivo, single or several molecules derive electrons with high efficiency. For this reason, the measurement of the electrical conduction through single or several cyt.c molecules in solid state is a challenge to a critical stage towards the realization of bioelectronic devices using electron transfer proteins. Here, we demonstrate that cytochrome c molecules are electrically active on electrode surface modified with self-assembled monolayer. We also found that the strong influence of the variation of self-assembled monolayer on the conduction through cytochrome c. The gap-edge voltages observed are 0.5V for 2,2â?T-PySSPy and 1.3V for 4,4â?T-PySSPy. To confirm the participation of heme in the conduction through cytochrome c, the comparative experimenht for Zn cytochrome c, whose heme ion of Fe is replaced to Zn, was performed. In case of Zn cytochrome c, any detectable current has not been observed. This implies that the current goes through the ion in the reaction center of cytochrome c molecules suggesting that the conduction mechanism might be single electron tunneling. The SAM modification is also useful for nanogap electrode. The current through the molecule increases with increasing temperature suggesting the presence of thermal excitation.

10:40am **EM1-ThM8 Tunneling Transport through Benzoate on Cu(110)*, *D.B. Dougherty,*** *P. Maksymovych, J.T. Yates Jr.,* University of Pittsburgh

The possible use of single molecules as devices in electronic circuits requires a fundamental understanding of the influence of the details of the linkage and charge transport to a macroscopic contact. Molecular orientation, chemical bond strength and location, and energetic location of molecular orbitals may all play a role in determining the possible use of a given molecule/contact system. Thus, detailed experimental studies of simple molecules in well-defined and reproducible configurations are necessary to supplement and guide more technologically relevant work. Significant progress has been made in understanding the transport properties through long chain molecules linked to Au surfaces by a thiolate group.@footnote 1@ These linkages are not the only potentially interesting candidates for electronics. In fact, the enormous chemical variety available is one of the great advantages of using organic molecules in devices. We have studied the electronic transport properties of benzoate molecules on a clean Cu surface which are linked by a carboxylate group instead of a thiolate.@footnote 2@ Such a linkage can be strong and surface-site specific and may therefore result in useful and reproducible electrical contact. More importantly, it provides a tool for addressing fundamental issues in single molecule transport. Using scanning tunneling spectroscopy, we have measured the I/V and conductance characteristics of differently oriented benzoate molecules chemisorbed on a Cu(110) surface. Benzoate molecules adsorbed with their plane perpendicular to the surface have a diminished conductivity in the low bias regime when compared to molecules with their plane parallel to the surface. The conductivity is found to be independent of temperature. *Supported by the W.M. Keck Foundation and a Japanese NEDO grant. @FootnoteText@ @footnote 1@ W. Wang et al., Rep. Prog. Phys. 68 (2005) 523.@footnote 2@ B.G. Frederick et al., Surf. Rev. Lett. 3 (1996) 1523.

11:00am **EM1-ThM9 Hopping Transport through Self-Assembled Monolayer on a GaAs Surface*, K. Lee,*** Purdue University

In organic solids, hopping transport is known to be a primary conduction mechanism. The prominent feature of hopping transport is its low mobility, which has been major limitation of utilizing organic solid as an active channel material. However, it has been known@footnote 1@ that, with efficient @pi@-@pi@ stacking of @pi@-conjugated molecules, the mobility of organic solids can be dramatically improved. To realize this idea, highly pure single crystals of organic molecules have been used to demonstrate much higher mobility,@footnote 2@ but it is questionable whether it would be feasible to fabricate a 3-terminal device with reasonable operating voltage. Another suggested solution is to use well-ordered self-assembled monolayer (SAM) of @pi@-conjugated molecules as an active channel component. In this study, a testbed for hopping transport through SAM has been fabricated using back-to-back schottky diode structure on semi-insulating GaAs. Before depositing molecules, pre-deposition current is less than 1nA. After forming SAM on GaAs surface, significant change in conductivity was observed in several molecules. For instance, thiophenol SAM increased conductivity by ~10 times, whereas ODT SAM suppressed bulk leakage current by one third. There are two possible conduction paths that can explain this conductivity increase: 1) hopping conduction through SAM 2) surface potential change due to the molecular dipole moments. However, it is not likely that the second possibility is a primary reason for enhanced conductivity because of the fact that ODT SAM, which has relatively strong molecular dipole moment but no @pi@-electrons, decreased conductivity. In addition, the dependence of mobility on temperature indicates that hopping transport is dominant. Finally, the application of the testbed to chemical sensors and organic transistors will be discussed. @FootnoteText@ @footnote 1@ J. L. Bredas, et al., PNAS, 99, 5084 (2002)@footnote 2@ Vikram C. Sundar, et al., Science, 303, 1644 (2004).

11:20am **EM1-ThM10 Charging and Discharging Nanoscale Domains in Thin Films of Arylamines Studied with Kelvin Probe Microscopy***, J. Sun, S.C. Blackstock,* ***G.J. Szulczewski,*** University of Alabama

The work reported here was motivated to assess the feasibility of a non-volatile molecular memory based on charge storage in amorphous thin films. Toward that end, thin films of a series of redox-gradient arylamines were vapor deposited on oxidized p-type Si(100) wafers and subsequently charged in tapping mode with a voltage applied to a metal-coated AFM tip. The redox-gradient is designed to facilitate one-way electron transfer from the periphery of the molecule to its core. The concept is realized by synthesizing molecules with an easy to oxidize (i.e. ionize) moiety at the interior of molecule and surrounding it with harder to oxidize redox moieties.@footnote1@ In effect the gradient acts as a charge funnel toward the interior of the molecule. The extent of charging was measured with Kelvin probe microscopy (KPM). The charged domains have an apparent diameter of about 200 nm in the KPM image, which is larger than the real area due to the long-range interaction of the charge and the tip/cantilever. The charge half-life was proportional to the magnitude of the redox-gradient. For example, amines without a redox gradient discharged within 1 hour. In contrast, amines with a redox-gradient of ~0.8 eV could retain 50% of their initial charge after 10 hours. The charging is reversible. By applying a negative bias on the KPM tip the charged region could be neutralized. Although the charge is stable for many hours and can be neutralized, there is diffusion of charge in the films due to Coulombic repulsion. @FootnoteText@ @footnote1@ T. D. Shelby and S. C. Blackstock, "Preparation of a Redox-gradient Dendrimer. Polyamines Designed for One-Way Electron Transfer and Charge Capture" J. Am. Chem. Soc. 1998, 120, 12155.

11:40am **EM1-ThM11 Observation of trans-to-cis in Azobenzene by Spatially Resolved Scanning Tunneling Spectroscopy*, B.-Y. Choi,*** Seoul National University, Korea*; S.-J. Kahng,* Korea University, Korea*; Y. Kuk,* Seoul National University, Korea

There have been serious efforts to apply various organic molecules to an organic based memory. These molecules change their configuration by a charge transfer between surrounding bonds or to reach an energy minimization state when a bias voltage is reached at a certain voltage. Similar but slightly different organic molecules, photo sensitive molecules, may be used for this application. Scanning tunneling microscopy/spectroscopy experiment was performed on azobenzene single molecule adsorbed on a Au(111) surface in UHV at 5K. Azobenzene has two stereoisomers; trans- and cis-azobenzene which can be transformed to each other by UV irradiation or thermal energy. We could induce the trans-to-cis transition of a single trans-azobenzene by injecting electric pulses by using STM tip and the electronic structure of them were observed in sub-atomic resolution. The tip bias for the trans-to-cis transition is ~1.5V and cis-azobenzene returned back under negative tip bias or in time at the adsorption site. The LUMO state of trans-azobenzene was confined mainly within the benzene segments which were lying parallel to gold substrate. The HOMO state was localized within the nitrogen. Cis-azobenzene shows several spectroscopy results depending on the molecule-surface configuration. We also observed an LDOS of azobenzene on NaCl layers deposited on Cu(111). Adsorbed on NaCl, the azobenzene shows an electronic states which are not coupled to that of the metal surface.

Electronic Materials and Processing
Room 310 - Session EM2-ThM

Heteroepitaxy and Low-Dimensional Structures

Moderator: R.S. Goldman, The University of Michigan

8:20am **EM2-ThM1 Materials Integration of III-V Heterostructures***, **M. Goorsky**, S.L. Hayashi, A. Noori,* University of California, Los Angeles*; R.S. Sandhu,* University of California, Los Angeles and Northrop Grumman Space Technology*; A. Cavus, C. Monier, M. Lange, M. Wojtowicz, T. Block, A. Gutierrez-Aitken,* Northrop Grumman Space Technology **INVITED**

III-V wafer bonded structures satisfy requirements for electronic device structures that simultaneously possess a large surface lattice parameter (e.g., near that of InAs) and a high substrate resistivity. The objectives of the research are to address the fabrication of III-V composite wafer bonding with the ultimate goal of producing virtual substrates for advanced III-V devices. Graded buffer layers are one key technological step. Very thin InAlAs graded buffer layer structures were produced for virtual InAlAs substrate applications. The rapid kinetics of strain relaxation in In@sub x@Al@sub 1-x@As graded buffer layers (GBLs) was exploited to produce thin (0.21 µm - 0.90 µm) buffer layers graded from the InP substrate to 6.0 Å. GBL layers as thin as 0.21 µm showed full strain relaxation and GBL layers as thin as 0.45 µm showed similar growth mode, surface roughness, and strain relaxation as thicker GBL structures. The threading dislocation density was low (mid-10@super 6@ cm@super -2@) for the 0.45 µm and the 0.90 µm buffer layers but there was evidence of non-uniform threading dislocation distribution for the 0.21 µm buffer structures. The feasibility of aggressive grading for other III-V systems will also be addressed. For some applications, even a thin GBL - upon which device structures are grown - is not feasible for device applications. To address the issue of limited GBL thickness, hydrogen exfoliation ("Smart-Cut") has been assessed to transfer thin films of InP, InAs, or 6.0Å lattice parameter layers to high resistivity substrates. We have developed a strategy for implantation and exfoliation based on the nucleation and growth of mechanical cracks at the projected range of the implant. This method has led to reproducible exfoliation and successful transfer of a wide variety of semiconductor materials. Damage-free chemical-mechanical polishing (CMP) has also been developed to produce low roughness (< 1 nm r.m.s) surfaces for subsequent epitaxial deposition. Another issue associated with composite wafers is the coefficient of thermal expansion (CTE) differences between the bulk substrate and the transferred layer. We have incorporated the temperature-dependent CTE values into force-balance equations to determine the thermodynamic stability of heterostructures based on these materials. The stability criteria have been experimentally confirmed. Examples of device structures on graded buffer layers and transferred layers will be shown to demonstrate the feasibility of this approach for the integration of III-V heterostructures.

9:00am **EM2-ThM3 Interfacial Bond Formation in W-structured type-II IR Detectors as Revealed by Cross-Sectional Scanning Tunneling Microscopy***, **J.C. Kim**, J.G. Tischler, I. Vurgaftman, J.R. Meyer, E.H. Aifer, L.J. Whitman,* Naval Research Laboratory*; C.L. Canedy, E.M. Jackson,* SFA Inc.

W-structured type-II superlattices (W-SLs) were originally developed to enhance the gain of mid-wave infrared lasers, but also have desirable properties for the design of infrared detectors. We are currently investigating ternary (and quaternary) W-SL structures composed of InAs, InGaSb (InGaAsSb), and AlInSb (AlInAsSb) layers for use in long-wave and very long-wave infrared photodiodes. Interfaces play a significant role in W-SLs because there are twice as many interfaces in each period than in a typical two-constituent SLs such as InAs/Ga(In)Sb, and therefore more options to engineer interfaces in order to compensate strain. We use x-ray diffraction to determine the overall strain in the W-SLs, and cross-sectional scanning tunneling microscopy (XSTM) to directly image the atomic-scale structure of the SLs, including the interfacial bonds, as a function of growth conditions. Differences in the local bond length of different interfaces (e.g., AlAs vs. InSb) result in specific contrast in XSTM images, making it possible to directly identify the interfacial bond types. We find that "unforced" AlSb/InAs interfaces, where both shutters are switched simultaneously with the intention of creating a neutral mix of interfacial bonds, actually consist predominantly of AlAs bonds, leading to undesirable strain. In contrast, InGaSb/InAs interfaces form as intended. We will discuss the surface science underlying the formation of these interfacial bonds, along with their effects on the optical properties and device characteristics.

9:20am **EM2-ThM4 Control of InAs/GaAs Quantum Dot Density and Positioning Using Modified Buffer Layers***, **W. Ye**, S. Hanson, M. Reason, X. Weng, R.S. Goldman,* The University of Michigan

Recently, strain-induced self-assembled quantum dots (QDs) have enabled the development of high performance light-emitters and detectors. Further advances in optoelectronics and quantum computing will require a narrowing of the density of states and achievement of periodic charge distributions, both of which necessitate the fabrication of high density, nearly monodispersed, highly ordered QD arrays. Various efforts have been made to achieve high densities of laterally ordered InAs/GaAs QDs. However, the mechanisms of lateral ordering of QDs are the subject of continued debate. A significant remaining question concerns the effects of buffer layers on the QD density and lateral ordering. Therefore, we have examined the patterning effects of buffer layers during the growth of QD SLs. Our QD SLs consisted of 2.6 ML InAs and 5 nm GaAs grown by molecular beam epitaxy at 500°C. Prior to QD deposition, GaAs buffer layers were grown under several different conditions, involving growth and/or annealing at 580°C and 500°C. High temperature grown buffers consist of relatively flat surfaces, while lower temperature grown buffers contain "mound-like" features elongated along the [1-10] direction. Isotropic distributions of QDs are observed for QD growth on flat buffers. Interestingly, QD alignment along the [1-10] direction is observed for QD SL growth on buffers containing mounds. This anisotropic QD alignment is enhanced as the number of QD SL increases and is dependent on the density of mounds. For flat buffers, the density of QDs decreases with stacking, consistent with the model of Tersoff. However, for buffers containing mounds, this effect is compensated by an increase in QD density. We propose a new mechanism for QD nucleation, which is based upon patterning by undulated In-enriched GaAs spacer layers following the initials sets of QD SLs.

9:40am **EM2-ThM5 Implantation-Defect-Mediated Intermixing of InAs/InP Quantum Dot Layers***, **C. Dion**,* École Polytechnique de Montréal, Canada*; S. Raymond, G. Ortner, P.J. Poole,* National Research Council of Canada, Canada*; F. Schiettekatte, M. Chicoine,* Université de Montréal, Canada*; P. Desjardins,* École Polytechnique de Montréal, Canada

The reduced dimensionality provided by quantum dots (QDs), which leads to atom-like discrete energy levels and @delta@-function-like density of states, offers possibilities for considerable improvements in optoelectronic device applications. However, the use of these nanostructures relies on achieving precise tunability of QDs luminescence emission through QDs size and composition. Since InAs/InP QDs growth is complicated by the rapid exchange of group V species at the InAs/InP interfaces, a post-growth method to fine tune the electronic properties of this particular system is of great relevance. We have investigated the effect of post-growth P implantation followed by rapid thermal annealing on the low-temperature photoluminescence (PL) spectra of self-assembled InAs/InP(001) QDs grown by chemical beam epitaxy (CBE) and metal-organic vapor phase epitaxy (MOVPE). In untreated samples, threshold temperature for intermixing was found to be 725 °C with blueshifts of the PL peaks of up to 90 meV after RTA at 800 °C for 210 s, while preserving emission bandwidth. In order to obtain larger blueshifts, we studied the effect of introducing point defects into InP cap layers by implanting P at energies sufficiently low to insure that the InAs QDs were not damaged. Implantation with fluence as low as 10@super 12@ P/cm@super 2@ followed by annealing at 500 °C were sufficient to induce a 275 meV blueshift. These observations give important insights into the role of defects generated in InP-based structures on the As/P intermixing and reinforce the applicability of ion implantation for the fabrication of monolithically integrated devices. Implantation-defect-mediated intermixing for wavelength tuning of InAs/InP QDs-based laser structures was investigated.

10:00am **EM2-ThM6 Modeling of InAs/GaAs Self-Assembled Heterostructures: Quantum Dot to Quantum Ring Transformation***, **I. Filikhin,*** North Carolina Central University*; E. Deyneka,* North Carolina A&T State University*; B. Vlahovic,* North Carolina Central University

It is possible to directly observe discreet energy spectra of self-assembled quantum dots (QD) and quantum rings (QR) by means of capacitance-voltage (CV) spectroscopy.@footnote 1,2@ Related theoretical studies, however, had some difficulties interpreting the experiments. Acquired values of the electron effective mass in QD@footnote 1@ and QR@footnote 2,3@ were significantly larger than the bulk mass. Also, the value of the energy-gate-voltage conversion coefficient was in disagreement with experimental conditions.@footnote 2,3@ In presented work we use relatively simple single subband model for InAs/GaAs QD(QR) where the energy dependence of electron effective mass is defined by the Kane formula.@footnote 4@ Model assumptions lead to the non-linear Schrodinger equation in 3D space.@footnote 5@ Model geometrical parameters are based on the fabrication process for InAs/GaAs QD/QR,@footnote 6@ for which the experimental CV data is available.@footnote 1,2@ We assume that the QD to QR transformation occurs without the loss of InAs material. Energies of confinement states of QD(QR) are calculated. Obtained results for single energy levels are in good agreement with the CV spectroscopy.@footnote 1,2@ Our calculations reproduce experimental value for the energy-gate-voltage conversion coefficient as 7. Magnitude of the non-parabolic contribution to the electron effective mass is also evaluated. @FootnoteText@ @footnote 1@ B. T. Miller, et al., Phys. Rev. B 56, 6764 (1997).@footnote 2@ A. Lorke, et al., Phys. Rev. Lett. 84, 2223 (2000).@footnote 3@ A. Emperador, et al., Phys. Rev. B. 62, 4573 (2000).@footnote 3@ E. Kane, J. Physics and Chemistry of Solids 1 249 (1957).@footnote 4@ Li Y, et al., Journal Applied Physics 90 6416 (2002).@footnote 5@ I. Filikhin, E. Deyneka and B. Vlahovic, Model. Simul. Mater. Sci. Eng. 12, 1121 (2004).@footnote 6@ J.M. Garsia et al., Appl. Phys. Lett. 71, 2014 (1997).

10:20am **EM2-ThM7 Relaxed Coupling Conditions between Quantum Dots and Photonic Crystals***, **P. Petroff,*** University of California, Santa Barbara **INVITED**

The possibility of controling the photon emission directionality and enhancing their emission rate by using quantum dots (QDs) coupled to a high Q photonic crystal (PC) opens important technological applications e.g. single photon emitters and detectors. Hence, understanding and controling this coupling is essential if the weak or strong coupling regime is to be routinely achieved. Coupling conditions are however, very demanding, since both the position of the QD and its frequency must be tuned to the PC the mode location and the ultra sharp resonant frequency. We will demonstrate using the InAs/GaAs system a strategy which allows for the deterministic coupling of a single QD to an S1 PC. This technique is general and can be applied to other PC types.@footnote 1@ We report high Purcell factors and non-trivial relaxation dynamics for off resonance lines in all fabricated structures.. We will discuss the coupling of an L3 PC with a dilute InAs/GaAs QD system which shows an ultra low threshold stimulated emission. This "threshold-less" laser is realized even for off -resonance coupling conditions between the QDs and the L3-PC. This new body of experimental observations suggests a relaxation of the coupling conditions which is specific to the QDs. We will present evidence that the continuum of states associated with the wetting layer together with acoustic phonons are involved in these relaxed coupling conditions. Acknowledgments: This work has been carried out in collaboration with A. Badolato, K. Hennessy, S. Strauf, M. Atature, J. Dreiser, M. Rakher, L. Andreani, E.Hu, A. Imamoglu and D. Bouwmeester. The support of an NSF-NIRT no: 0304678 and DARPA no: 972-01-1-0027. @FootnoteText@@footnote 1@A.Badolato et al., Science 308, 1158 (2005).

11:00am **EM2-ThM9 Formation of Flat, Relaxed Si@sub 1-x@Ge@sub x@ Alloys on Si(001) Without the Use of Buffer Layers***, **S. Hong**, H.-W. Kim, D.K. Bae, S.C. Song, G.-D. Lee, E. Yoon,* Seoul National University, South Korea*; C.S. Kim,* Korea Research Institute of Standards and Science*; Y.L. Foo, J.E. Greene,* University of Illinois at Urbana-Champaign

Flat, fully-strained Si@sub 1-x@Ge@sub x@ layers with thicknesses ranging from 40 to 240 nm were grown on Si(001) at 450 @super o@C by ultrahigh vacuum chemical vapor deposition and subjected to furnace annealing at 1000 @super o@C for 20 min to induce relaxation. In order to suppress the thermally-activated surface adatom diffusion leading to surface roughening, while simultaneously promoting misfit dislocation formation, SiO@sub 2@ capping layers were deposited prior to annealing. The degree of strain relaxation R and the root-mean-square surface roughness w are determined as a function of layer thickness. For Si@sub 1-x@Ge@sub x@ layers annealed without SiO@sub 2@ cap layers, the primary relaxation mechanism is strain-induced roughening leading to the formation of a self-organized mound structure with high w and R. However, for capped layers, strain-relaxation occurs through the formation of misfit dislocations and surface roughening is controlled by the resulting cross-hatch. Detailed analysis using atomic force microscopy line scans show that the crosshatch patterns consist of slip steps produced by misfit dislocations at the Si@sub 0.77@Ge@sub 0.23@/Si(001) interface. The presence of oxide cap layers during annealing changes the mechanism of strain relaxation from strain-induced to misfit dislocation induced roughening and inhibits surface diffusion such that the evolution of crosshatch ridges from slip steps is limited. As a result, with oxide capped 240-nm-thick films, we obtain smooth, relaxed Si@sub 0.77@Ge@sub 0.23@ layers with w = 0.68 nm and R = 68% without the necessity of using several-µm-thick compositionally-graded buffer layers.

11:20am **EM2-ThM10 Formation of Epitaxial Ge Nanorings on Si by Self-assembled SiO@sub 2@ Particles and Touchdown of Ge Through a Thin Layer of SiO@sub 2@***, **Q. Li**, S.M. Han,* University of New Mexico

We demonstrate that hexagonally packed single-crystalline Ge rings can be grown around the contact region between self-assembled SiO@sub 2@ spheres and 1.2-nm-thick chemical SiO@sub 2@ on Si. When the oxide-covered Si substrate is pulled from a colloidal suspension of SiO@sub 2@ spheres, the SiO@sub 2@ spheres self-assemble into a hexagonally packed monolayer on the substrate. These SiO@sub 2@ spheres provide a surface diffusion path to guide the Ge adspecies to reach the substrate. We have previously determined that the Ge adspecies readily desorb from the bulk SiO@sub 2@ surface with a desorption activation energy of 42±3 kJ/mol. This low desorption activation energy gives rise to a low surface diffusion barrier, which in turn leads to a high diffusion length on the order of several micrometers, exceeding the dimension of the SiO@sub 2@ spheres. With a flux of Ge impinging at 45° from the surface normal, the Ge beam cannot directly impinge on the underlying substrate through the openings between SiO@sub 2@ spheres. The Ge adspecies diffuse around the SiO@sub 2@ spheres and "touchdown"[Li et al., APL, 85(11), 1928 (2004)] through the chemical SiO@sub 2@, forming epitaxial ring structures. The touchdown process anchors nanoscale Ge seed pads to the underlying Si substrate. The ring formation uniquely takes advantage of the SiO@sub 2@ sphere self-assembly; the weak interaction between Ge adspecies and SiO@sub 2@; and the touchdown where Ge densely nucleate on Si surface through the 1.2-nm-thick chemical oxide. We will also demonstrate that ring dimension and geometrical arrangement can be precisely controlled by the size of the SiO@sub 2@ spheres and by the artificially introduced surface corrugation, respectively.

11:40am **EM2-ThM11 Local Origins of Catalytic and Sensor Activity in 1D Oxide Nanostructures: From Spectromicroscopy to Device***, **A. Kolmakov**,* SIUC*; U. Lanke,* University of Saskatchewan, Canada*; S.V. Kalinin,* Oak Ridge National Laboratory

When nanowire radius (or nanobelt's thickness) is comparable with its Debye length, the adsorption/desorption of donor/acceptor molecules on the surface of the nanowire (nanobelts) drastically alters the bulk electron density inside the nanowire manifesting superior performance of nanostructure as a chemical sensor as an example. For the nanostructures which are functionalized with catalytic particles this appears to be an oversimplified picture. The sensing effect of such 1-D metal oxide chemiresistor or chemi-FET can have completely different origins like spillover effect from catalyst particles, gas induced barrier modulations of the local electroactive element (nanoparticles, defects etc)or transient processes in the gate oxide. To explore the relative importance of these phenomena on catalytic and sensing performance of 1D nanostructures, adsorbate specific, microscopic techniques have to be developed. We have tested a range of imaging techniques to address local transport behavior in the working metal oxide nanostructure wired as chemiresitor and chemi-FET. In particular, we have developed the experimental techniques and preparative protocols for implementation of synchrotron radiation based spectro-microscopies (SPEM and X-PEEM) to individual 1D nanostructures. Using X-PEEM in NEXAFS mode we demonstrated the ability to reveal submicron lateral compositional and electronic (work function) inhomogeneouties in individual nanowire. We were also complemented our results with Scanning Impedance Microscopy (SIM) and Scanning Surface Potential Microscopy (SPPM) to acquire ac and dc potential distributions in an operating nanowire device. These results open new avenue to visualize the adsorption /desorption phenomena on the surfaces of the individual nanostructure both in real time and at nano- and mesoscopic level.

Magnetic Interfaces and Nanostructures
Room 204 - Session MI+MS+NS-ThM
Advanced Magnetic Storage and Manufacturing Processes

Moderator: E.A. Dobisz, Hitachi Global Storage Technologies/San Jose Research Ctr.

8:20am **MI+MS+NS-ThM1 Interface Stability between Amorphous Ferromagnetic Layer and Oxide Barriers in Tunneling Magnetoresistive Films at Elevated Temperatures***, **X. Peng**, D. Kvitek, A. Morone, E. Granstrom, S. Xue,* Seagate Technology

Interface stability and microstructure between amorphous ferromagnetic (FM) layers Fe@sub 56@Co@sub 24@B@sub 20@ (atomic percent), and oxide barrier layers (AlO) as deposited by physical vapor deposition, in both as-deposited and annealed states, have been studied using magnetic measurement by looper, elemental depth profiling by X-ray Photoelectron Spectroscopy (XPS), and atomic level microstructure by Transmission Electron Microscopy (TEM) respectively. AlO is amorphous on both amorphous Fe@sub 56@Co@sub 24@B@sub 20@ and crystalline FM layers. Substantial Fe diffusion towards the AlO layer and Al towards FM layer are clearly observed for Fe@sub 56@Co@sub 24@B@sub 20@/AlO system for annealing beyond 360°C, and will likely cause the MTJ devices made from this system to not functioning.

9:00am **MI+MS+NS-ThM3 Nanoimprint Technologies for Magnetic Recording Media***, T. Ando, **C. Haginoya**, K. Kuwabara, M. Ogino, K. Ohashi, A. Miyauchi,* Hitachi Ltd., Japan **INVITED**

The discrete-track and patterned media have been developed as future magnetic recording media.@footnote 1,2,3@ Nano-scale patterns are formed on the disk surface of these media. The fine patterning technologies are required for producing the patterned disks. The nanoimprint technology is attractive for the fabrication of nano-scale structures in view of cost and mass production. There are two main types of the nanoimprint technologies. One is the thermal nanoimprint technology that fine structures are formed on thermoplastic polymer layer. Another is the photo nanoimprint technology that ultra-fine structures are formed on photo-curable polymer layer. There are several key points for media application such as pattern formation area, resolution, precise control of pattern transfer, lifetime of nano-mold, alignment and so on. The pattern formation area is important for producing patterned disks. We developed a thermal nanoimprint machine that has the auto-parallel system, two step pressure system and so on. The machine enabled us to imprint fine dots on a 300 mm diameter Si wafer using a 300 mm diameter mold. The pattern formation area is large enough to produce the 65 mm diameter patterned disks. The fine resolution is required for high recording density. Austin et al. formed 6 nm half-pitch structure using supperlattice stamper,@footnote 4@ and this resolution seems enough for Tbpsi storage era. D. Wachenschwanz et al.@footnote 1@ and Y. Soeno et al.@footnote 3@ evaluated write/read performance of the discrete-track media that the grooves and servo patterns were formed by using thermal nanoimprint and etching processes. Nanoimprint is promising way for discrete-track and patterned media. @FootnoteText@@footnote 1@ D. Wachenschwanz et al., INTERMAG 2005, no. BB02 @footnote 2@ B.D. Terris et al., INTERMAG 2005, no. BB03 @footnote 3@ Y. Soeno et al., INTERMAG 2005, no. FR04 @footnote 4@ M. D. Austin et al., 3rd Conf. on Nanoimprint Nanoprint Technology 2004, no. III.2

9:40am **MI+MS+NS-ThM5 Ultra Narrow Magnetic Recording Heads: Processing Challenges***, **M.-C. Cyrille**,* HITACHI Global Storage Technologies - San Jose Research Center **INVITED**

As the areal density of magnetic recording increases well beyond 100Gb/in2, the critical dimensions of recording heads continue to shrink at a rate of 30% per year.@footnote 1@ Today, thin film heads with 100nm or less critical dimensions are being routinely fabricated in manufacturing. By the end of 2006, the physical trackwidht of read head sensors is expected to be less than 60nm. The industry is turning to Direct write E-beam and DUV 193nm as the lithography tools of choice to meet those small dimensions. As the material set used to fabricate thin film magnetic heads is unique to this technology, specific challenges arise when trying to pattern such small devices without loss of performances. Damage due to standard patterning techniques can be now be observed on both the reader and the writer as their dimensions become smaller than 100nm and advances in tooling and processes tailored to each kind of magnetic sensor are required to overcome this issue. @FootnoteText@@footnote 1@ Fontana R.E., MacDonald S.A., Santini H, Tsang C., IEEE Trans. Mag 35, 806 (1999)

10:20am **MI+MS+NS-ThM7 Correlated AFM/MFM and Magneto-Optical Studies on Epitaxial L1o FePd Thin Films***, R.A. Lukaszew, M. Mitra, **J. Skuza**,* University of Toledo*; A. Cebollada-Navarro, J.M. Garcia-Martin, C. Clavero Perez,* Institute of Microelectronics in Madrid (IMM) - Spain

The latest trend in data storage exploits perpendicular recording. Magnetic binary alloys (e.g. Fe-Pd, Fe-Pt) are of significant interest in magneto-recording because highly ordered L1o structures of these alloys exhibit very large magnetic anisotropy that can withstand the super-paramagnetic limit when reduced in size to accommodate the projected demands for higher areal densities. They can be deposited as films with the anisotropy axis perpendicular to the film plane, making them suitable for perpendicular media. There are practical problems associated with this scheme because usually the experimentally achieved perpendicular anisotropy tends to be too large for writing on this media. Therefore it has been suggested that canted magnetization would be more appropriate. Here we show our correlated XRD, AFM/MFM and magneto-optical studies on two series of epitaxial L1o FePd thin films of varying thickness grown on MgO. We have observed that the choice of capping material has significant effect on the resulting magnetic and magneto-optical properties of the films. We will show correlated structural and magneto-optical data for films grown under identical conditions but capped with either MgO or Pd. Our studies demonstrate that in the first case the films exhibit strong perpendicular anisotropy while in the latter the films have a magnetization component along the plane of the films in addition to the perpendicular component, thus yielding a net canted magnetization. In addition the films capped with Pd exhibit smaller coercivities than the ones capped with MgO thus enhancing their prospect use in heat-assisted magneto-recording.

10:40am **MI+MS+NS-ThM8 Magnetic Properties of Epitaxial FeN Thin Films***, R.A. Lukaszew,* University of Toledo*; R. Gonzalez-Arrabal,* University Autonoma of Madrid, Spain*; **C. Sanchez-Hanke**,* Brookhaven National Laboratory*; R. Loloee,* Michigan State University*; D. Boerma,* University Autonoma of Madrid, Spain

Low anisotropy and low magnetostriction iron based FCC films are attractive candidate materials for inductive thin film write heads in magnetic recording. Currently these are made of permalloy and other Fe alloys with polarization ranging from 1.0-1.6 T. Higher polarization is needed to create sufficient stray field to write on the higher-coercivity media that is needed as head and bit dimensions decrease to allow higher areal densities. Fe-N has been proposed as a possible material for the sensing element in read-head. Fe-N exhibits a variety of phases, some of which have enhance magnetic moment. In particular the meta-stable @alpha@"- Fe16N2 is particularly interesting because has the largest saturation magnetization reported of all known materials. We will present a comparative experimental study on epitaxial Fe-N thin films with varying degrees of @alpha@", @alpha@' and @gamma@' phases. The films were obtained using either sputtering or MBE. In the latter case, the films were grown in the presence of a N flow and the growth conditions were optimised in order to obtain a high content of @alpha@"- Fe16N2. A variety of characterization techniques was used to establish the epitaxial character of the films as well as the amount and kind of phase present. The magnetic properties of the samples was characterized by element specific X-ray Magnetic Circular Dichroism (XMCD).

11:00am **MI+MS+NS-ThM9 Processing Technology for Magnetic Random Access Memory***, **M.C. Gaidis**, J.P. Hummel, S.L. Brown, S. Kanakasabapathy, E. O'Sullivan, S. Assefa, K. Milkove, D. Abraham, Y. Lu, J.N. Nowak, P. Trouilloud, D. Worledge, W.J. Gallagher,* IBM **INVITED**

Magnetic Random Access Memory (MRAM) offers the potential of a universal memory - it can be simultaneously fast, nonvolatile, dense, and high-endurance. Depending on application, these qualities can make MRAM more attractive than SRAM, DRAM, flash, and hard drive memories, with a market measured in the billions of dollars. Small-scale demonstrations have realized much of the potential of MRAM, but scaling the memory to production on economically-profitable 200 or 300 mm wafer sizes creates unique processing challenges heretofore unseen in a large-scale semiconductor fabrication facility. MRAM read operations rely on electron tunneling through a thin (1 nm) insulating barrier between magnetic films. The exponential dependence of tunnel current on barrier thickness imposes requirements for across-wafer film uniformity on the order of 0.01 nm, made possible only by recent developments in deposition technology. To maximize performance, typical magnetic film stack designs can incorporate more than 10 distinct film layers. Very few of these layers can be etched by semiconductor-industry-standard RIE processes, and thus have required development of novel patterning techniques specifically tuned to minimize corrosion and to handle the nonvolatile nature of etch byproducts. The elements in these complex film layers tend to interdiffuse at temperatures below that of back-end-of-line (BEOL) semiconductor processing, thus necessitating the development of low-temperature processes for creating the BEOL wiring and packaging. Although daunting, each of the aforementioned challenges has largely been overcome. This presentation provides an overview of the basic MRAM structure and operation, followed by a discussion of the MRAM-specific processing techniques that have been developed to realize this technology in megabit arrays on 200 mm wafers.

Nanometer-Scale Science and Technology
Room 210 - Session NS-ThM

Nanotube-based Devices

Moderator: S. Evoy, University of Alberta, Canada

8:20am **NS-ThM1 Quantum-dot Nanodevices with Carbon Nanotubes***, K. Ishibashi, S. Moriyama, T. Fuse, D. Tsuya, M. Suzuki,* RIKEN, Japan **INVITED**

Carbon nanotubes are attractive building blocks for extremely small nanodevices. In this paper, we present our effort to fabricate and demonstrate quantum-dot nanodevices, which includes following topics. 1) Single electron devices: A single electron transistor (SET), a single electron inverter that is consisting of two SETs in series, and a single electron XOR that has two input gates to SET, are fabricated in individual single-wall carbon nanotubes (SWCNTs) or multi-wall carbon nanotubes (MWCNTs), and their operation was demonstrated. 2) Quantum computing device (Qubit) and an artificial atom in the SWCNT: We focus on the spin qubit in association with observations of the artificial-atom like behavior. It is shown that the four or two electron shell structure was observed in single electron transport measurements at milli-Kelvin temperatures, and the shell filling of successive electrons and the Zeeman splitting of single particle states were confirmed in the magnetic field evolution of each Coulomb peak. The simple singlet and triplet states were directly observed in excitation spectroscopy measurements when two electrons were contained in a shell. These observations show that the SWCNT is very similar to natural atom with its unique shell structure and an energy scale of submillimeter to THz ranges. Despite the demonstrated wonderful properties as a building block of the nanodevices, we should admit that a breakthrough of device processes suitable for carbon nanotubes is really needed to realize more reliable and reproducible nanodevices.

9:00am **NS-ThM3 Stable Electron Emission from a Multi-Wall Carbon Nanotube in Low Vacuum***, **H. Suga,*** Nihon University, Japan*; H. Abe, M. Tanaka,* National Institute of Advanced Industrial Science and Technology (AIST), Japan*; T. Ohno,* Technex Lab Co., Japan*; Y. Nishioka,* Nihon University, Japan*; H. Tokumoto, T. Shimizu,* AIST, Japan

Carbon nanotubes have been studied intensively in order to realize functional devices utilizing their unique electrical and mechanical properties. Then we have tried to fabricate the electron emitter using a multi-wall carbon nanotube (MWNT). Electrons are usually emitted applying several kilo volts to tungsten tip apex in ultra high vacuum. Therefore it is necessary to prepare high voltage power supply and expensive vacuum pumps like ion pumps. Then the aim of our research is to realize the MWNT electron emitter, by which electrons can be extracted at voltages lower than 500V in low vacuum around 10@super -3@ to 10@super -5@Pa. MWNT electron emitters are fabricated as follows. Tungsten wire and tungsten loop were spot-welded, the wire was electrochemically etched. Then metal nano particles were smeared on the etched tip. Using a specially designed nano-manipulator combined with SEM (Tiny-SEM (W380mmxD350mmxH600mm) by Technex in Japan), a MWNT was attached on the tip apex, at first by the electron beam induced carbon deposition, and, to further assure the bonding between the MWNT and the tip, smeared metal nano particles were melted by heating tungsten loop. Typical length and diameter of the fabricated emitters are about 5µm and 20nm, respectively. Furthermore, in the SEM, the field emission can be carried out and the emitter-anode plane distance can be easily controlled on a micrometer scale, which is typically about 20µm. We measured turn-on field of 5 V/µm which is lower than conventional tungsten emitter in UHV. The emission current of 0.1 to 0.3µA can be attained at applied voltage of 70 to 160V on the same low vacuum condition. The stability of emission current about 1.5% at 0.3µA can be gained. The new way of high stability and the brightness and lifetime evaluation can be discussed in detail in the presentation. @FootnoteText@ hiroshi-suga@@aist.go.jp, tetsuo-shimizu@@aist.go.jp

9:20am **NS-ThM4 Carbon Nanotubes as Ballistic Phonon Waveguides and Electro-Mechanical Switches***, **V. Deshpande**, H.-Y. Chiu, H. Postma, M. Bockrath,* California Institute of Technology

PART I: Carbon nanotubes' exceptional thermal conductivity suggests that they may serve as efficient heat conduits to aid in the cooling of nanoscale circuits. Here, we report ballistic phonon transport, which provides the ultimate limit for heat dissipation. Upon heating freestanding nanotube devices with an electrical current, we find that the power required for the nanotube to reach a particular temperature is independent of nanotube length for devices shorter than ~500 nm, and follows a universal scaling law in the tube radius. This provides evidence for ballistic phonon propagation and suggests that, over such length scales, the heat carrying capacity of nanotubes has only fundamental limits imposed by their 1D nature. From our data, we obtain an estimate for the quantum of thermal conductance that is in good agreement with the Landauer picture of phonon transport. We then present a coherent picture of nanotube breakdown based on the thermal activation of bond-weakening electronic transitions. Finally, we find that the efficient propagation of heat to the electrical contacts enables the contacts to be annealed and improved in-situ. PART II: NEMS devices are competitive in switching speed with electronic devices, because of their low mass and small size. We are developing relay devices using multi-walled nanotubes (MWNTs) that exploit the ability of concentric nanotube shells to act as low-friction linear bearings. Analysis of our data yields a measurement of the retraction force on the inner nanotube shells from the outer shells, which agrees with theoretically expected value. We are able to electrostatically telescope shells of a MWNT to establish electrical contact and turn the device to a conducting "on" state. The device can be turned "off" again by applying a sufficiently large gate voltage to bend the nanotube segments until the connection is broken. Possible applications include memories, logic gates, and high-gain nanomechanical amplifiers.

9:40am **NS-ThM5 Carbon Nanotube Transistors and How They Are Different***, **J. Appenzeller**,* IBM Research Division, US **INVITED**

Over the last few years carbon nanotubes (CNs) have attracted an increasing interest as building blocks for electronics applications. While metallic nanotubes are considered as interconnects in integrated circuits, semiconducting tubes are evaluated as field-effect transistor (FET) components. Since the first CNFET operation has been demonstrated in 1998,@footnote 1,2@ device performance has been significantly improved.@footnote 3,4,5@ Among other things it has been shown that CNFETs operate in the ballistic regime even at room-temperature, provided that not too large drain and gate voltages are applied and that their channel length does not exceed a couple of hundred nanometers.@footnote 6,7,8@ One of the more unexpected findings in the context of CNFETs was that they cannot be described within a conventional MOSFET model. The most critical observation has been that carbon nanotube transistors in fact behave as Schottky barrier devices.@footnote 9,10@ It was found that switching in nanometer size semiconductors, such as carbon nanotubes, contacted with source/drain metal electrodes is determined entirely by the metal/semiconductor interfaces and their field-dependence, provided that transport in the semiconductor is ballistic. Making use of this particular type of nanotube property, we have been able to gain important insights into the topic of multi-mode transport in CNFETs@footnote 11@ and, most importantly, have recently successfully fabricated the first band-to-band tunneling CNFET with a much more abrupt switching behavior than can be obtained with any conventional transistor approach.@footnote 12@ @FootnoteText@ @footnote 1@ S.J. Tans A. Verschueren, and C. Dekker, Nature 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@ A. Bachtold, P. Hadley, T. Nakanishi, and C. Dekker, Science 294, 1317 (2001).@footnote 4@ A. Javey, H. Kim, M. Brink, Q. Wang, A. Ural, J. Guo, P. McIntyre, P. McEuen, M. Lundstrom, and H. Dai, Nature Materials 1, 241 (2002).@footnote 5@ S. Wind, J. Appenzeller, R. Martel, V. Derycke, and Ph. Avouris, Appl. Phys. Lett. 80, 3817 (2002).@footnote 6@ M. Fuhrer, H. Park, and P.L. McEuen, IEEE Trans. on Nanotech. 1, 78 (2002).@footnote 7@ A. Javey, J. Guo, Q. Wang, M. Lundstrom, and H. Dai, Nature 424, 654 (2003).@footnote 8@ S. Wind, J. Appenzeller, Ph. Avouris, Phys. Rev. Lett. 91, 058301 (2003).@footnote 9@ S. Heinze, J. Tersoff, R. Martel, V. Derycke, J. Appenzeller, and Ph. Avouris, Phys. Rev. Lett. 89, 106801 (2002).@footnote 10@ J. Appenzeller, J. Knoch, V. Derycke, R. Martel, S. Wind, and Ph. Avouris, Phys. Rev. Lett. 89, 126801

(2002).@footnote 11@ J. Appenzeller, J. Knoch, M. Radosavljevic, and Ph. Avouris, Phys. Rev. Lett. 92, 226802 (2004).@footnote 12@ J. Appenzeller, Y.-M. Lin, J. Knoch, and Ph. Avouris, Phys. Rev. Lett. 93, 196805 (2004).

10:20am **NS-ThM7 Carbon Nanotube Schottky Diodes for High Frequency Applications*, E.W. Wong*,** *H.M. Manohara, E. Schlecht, B.D. Hunt, P.H. Siegel,* Jet Propulsion Laboratory, California Institute of Technology

We have demonstrated Schottky diodes using semiconducting single-walled nanotubes (s-SWNTs) with titanium Schottky and platinum Ohmic contacts for high frequency applications. The devices demonstrate rectifying behavior with large reverse bias breakdown voltages of greater than -15 V. In order to decrease the series resistance, multiple SWNTs are grown in parallel in a single device, and the metallic tubes are burnt-out selectively. At low biases these diodes showed ideality factors in the range of 1.5 to 1.9. Results from devices containing multiple nanotubes suggest that these diodes can act as direct detectors at room temperature at 2.5 terahertz (THz) frequency with noise equivalent powers (NEP) potentially comparable to that of the state-of-the-art gallium arsenide sold-state Schottky diodes, in the range of 10@super -13@W/Hz@super 1/2@. In essence, the SWNT Schottky diodes with multiple parallel tubes per device with individually reduced resistances to the order of a few k@OMEGA@ promise superior performance compared to that of the state-of-the art solid-state Schottky diodes for applications at high frequencies.

10:40am **NS-ThM8 Study of High-Field Electron Transport in Multi-Wall Carbon Nanotubes by MCBJ Technique*, M. Tsutsui*,** *Y. Taninouchi, S. Kurokawa, A. Sakai,* Kyoto University, Japan

Multi-wall carbon nanotubes are foreseen to be a promising candidate for interconnects within atomic and molecular transistors owing to their high current carrying capacity. However, there still remain some controversies on high-field electron transport in MWNTs, in particular the conductance versus bias voltage (G-V) characteristics. In the present study, we have investigated high-field electron transport in MWNTs utilizing mechanically controllable break junction (MCBJ) technique. One of the advantages in this technique is that electrode gap distance can be manipulated with pico-meter resolutions after MWNTs being suspended between the electrodes. Bridging of MWNTs over Au electrodes is accomplished by repeatedly breaking Au contacts in a nanotube-dispersed solution. Measured G-V characteristics show that the conductance of MWNTs linearly increases with the bias up to 3 V. An important role of the nanotube/electrode contact resistance on the electron transport through MWNTs is suggested from G-V characteristics acquired at various electrode separations. Bias-polarity asymmetry is observed in Joule heating effects on nanotube/electrode contacts at high biases, and its implications will be discussed in the presentation.

11:00am **NS-ThM9 Enhancement on Field Emission Performance of MWNTs Impregnated with RuO@sub 2@ and Rooted into Metal Substrate*, H. Liu,*** The Graduate University for Advanced Studies, Japan*; T. Noguchi, K. Tatenuma,* KAKEN Inc., Japan*; S. Kato,* The Graduate University for Advanced Studies, Japan

We have shown that field emission characteristics of MWNTs are drastically enhanced by RuO@sub 2@ impregnation and MWNT rooting into a metal substrate. These new key technologies improve both increase of field enhancement factor due to a proper surface density of subnano and nano sized RuO@sub 2@ particles on MWNT surfaces and increase of electrical conductivity, thermal conductivity, high-temperature resistance and tensile strength due to their high adhesivity between MWNTs and the metal substrate. In this paper, we demonstrate that the electron emission current from bulky MWNTs could reach 1.2A/cm@super 2@ at 6.0V/µm and reach the maximum of 1.9A/cm@super 2@ at 7.5V/µm even in the continuous DC mode in optimization processes for the impregnation and the rooting. According to analysis of microscope images of the substrate, the results above can be corrected by a factor of 2.5 times considering that an area of 40% on the substrate was only covered with MWNTs because surface density of MWNTs on the substrate has not yet fully controlled in the process of the rooting. In the presentation, the detail of these results and discussions will be given with results of endurance running tests at the high current density.

11:20am **NS-ThM10 Topologically Induced Localized States in Single Wall Carbon Nanotubes*, S.-J. Kahng*,** Korea University, Korea*; S. Lee, H. Kim, J. Lee, Y. Kuk,* Seoul National University, Korea

The local electronic structures of semiconducting single wall carbon nanotubes was studied with scanning tunneling microscopy. We performed scanning tunneling spectroscopy measurement at selected locations on the center axis of carbon nanotubes, acquiring a map of the electronic density of states. Spatial oscillation was observed in the electronic density of states with the period of atomic lattice. Defect induced interface states were found at the junctions of the two semiconducting nanotubes, which are well-understood in analogy with the interface states of bulk semiconductor heterostructures. The electronic leak of the van Hove singularity peaks was observed across the junction, due to inefficient charge screening in a one-dimensional structure. Several paired, localized gap states were observed in semiconducting single-wall carbon nanotubes. A pair of gap states is found far from the band edges, forming deep levels. Another pair is located near the band edges, forming shallow levels. The deep levels are explained by a vacancy-adatom complex while the shallow levels are explained by a pentagon-heptagon structure. Our experimental observation indicates that the presence of the gap states provides a means to perform local band-gap engineering as well as doping without impurity substitution.

11:40am **NS-ThM11 Optimization of Impregnation of Subnano RuO@sub 2@ Clusters on MWCNT for Field Emission Displays*, T. Noguchi*,** *K. Tatenuma,* KAKEN Inc., Japan*; S. Kato,* High Energy Accelerator Research Organization (KEK), Japan

For applications of MWNTs to FEDs and the other electron sources, we reported the achievement of a remarkably high DC current density close to 300mA/cm@super 2@ with a threshold electric field of 2V/µm using a new technology of impregnation of subnano RuO@sub 2@ clusters on MWCNT surfaces and of MWNT rooting into a metal substrate. Here we focus on optimization of the impregnation for better electron emission property of MWNTs on ITO glass substrates. Preliminary investigation showed that two orders of magnitude less quantity of the impregnation was sufficient for MWNTs of high purity than MWNTs of low purity to obtain the same emission property. The quite different quantity of the impregnation for proper emission would be explainable based on possible absorption of RuO@sub 2@ particles into the impurities of MWNTs.

Plasma Science and Technology
Room 302 - Session PS+MS-ThM

Process Equipment Modeling

Moderator: D.J. Economou, University of Houston

8:20am **PS+MS-ThM1 Particle Modeling of Plasmas and Gases in Materials Processing*, K. Nanbu*,** *T. Furubayashi,* Tohoku University, Japan **INVITED**

The use of low gas pressure is a recent trend in plasma-assisted materials processing. The low gas pressure means that the collision frequency between two species are insufficient to recover the equilibrium in the velocity distributions. In such a case the particle modeling of plasmas and gases has more sense. First, it is shown that the particle modeling is a solution method of the Boltzmann equation. This gives the theoretical basis of the DSMC (direct simulation Monte Carlo method) for neutral gases and the PIC/MC (particle-in-cell Monte Carlo method) for plasmas. Second, the state-of-the-art modeling is discussed by introducing the problems thus far solved. Last, the results of two newly solved problems are given to show the feasibility of the particle modeling. One is the complicated gas flows in an etching apparatus, consisting of source gases Ar, C@sub 4@F@sub 6@, and O@sub 2@, radicals CF@sub 2@ and C@sub 3@F@sub 4@, and by-products SiF@sub 4@ and CO. The second is the self-sputtering of copper target. The species in the sputtering apparatus are electrons, ions, and sputtered atoms. Here we propose a method to simulate all these species simultaneously even though the velocity difference among species is disparate. This is the first application of the particle modeling to the problem where the slow neutral species are taken into consideration together with charged particles.@footnote 1@ @FootnoteText@ @footnote 1@ K. Nanbu, IEEE Trans. Plasma Science, Vol. 28 (2000), 971-990.

9:00am **PS+MS-ThM3 Coupled Analysis of Inductively-coupled CF@sub 4@ Plasmas and Radicals Flow*, H. Takekida*,** *K. Nanbu,* Tohoku University, Japan

Inductively-coupled CF@sub 4@ plasmas are widely used for the etching of oxide films. In the present work, plasma and flow in an inductively-coupled CF@sub 4@ plasma reactor are simulated simultaneously. The plasma structure and the production rates of CF radicals are examined using the Particle-in-Cell Monte/Carlo (PIC/MC) method. We included low frequency wafer biasing in the plasma simulation. The radicals flow is examined using the direct simulation Monte/Carlo (DSMC) method for which the production rate of CF@sub x@ radicals is the input data from the plasma simulation. The etching reaction on the oxide wafer and the etch products are taken into consideration in the DSMC. After the flow simulation is finished, plasma simulation is improved using the spatial distribution of background CF@sub 4@ gas which is derived from the flow simulation. We repeated a set of these plasma and flow simulation until we obtain a convergence. We compare the results with the ones where the density of background gas CF@sub 4@ is assumed to be uniform. We clarified the effect of gas flow on the CF@sub 4@ plasma structure by the use of coupled analysis. We have found that the radicals flow has a large effect on the spatial distribution of plasma density.

9:20am **PS+MS-ThM4 Effects of an Insulating Focus Ring on a Uniformity of Radical/Ion Distributions in a Wafer Interface in a 2f-CCP Etcher***, **T. Yagisawa**, T. Makabe,* Keio University, Japan

Technological improvement in efficiency of reactive ion etching of oxide film is still a main issue in plasma etching under the circumstances that the size of the wafer has been continuously increasing from 100 mm in diameter in 1975 to 300 mm in 2003, as well as the miniaturization of ULSI. The etch rate of SiO@sub 2@ in a fluorocarbon plasma is a function of the mixture between the accumulation of radical species on the surface and the impact energy of ions incident on the wafer. Through a series of numerical studies by using VicAddress in addition to the experimental ones, we have demonstrated that a 2f-CCP (two-frequency Capacitively Coupled Plasma) driven by VHF (100 MHz) and LF (1 MHz) sources at each of electrodes has the plasma structure and characteristics appropriate for dielectric etching. That is, in a well designed 2f-CCP, VHF source is prepared to produce a high density plasma and LF source for a high energy ions incident on the wafer. We have confirmed that the radial variation of etch profile is mainly caused by the strong distortion of the surface potential at the wafer edge. In the present study, the influence of the geometry (width and height) and the dielectric constant of the focus ring in SiO@sub 2@ etching has been investigated in CF@sub 4@(5%)/Ar from the viewpoint of the ion velocity (energy and angle) distribution and the radical flux incident on the wafer as a function of radial position. The effective area of the wafer to be processed will be improved by the design of the interfacial physical structure between the surface and the bulk plasma.

9:40am **PS+MS-ThM5 Simulation in Advanced Dielectric Etch Equipment Design and Process Tuning***, **K. Bera,** D. Hoffman, G.A. Delgadino, J. Carducci, Y. Ye, S. Ma,* Applied Materials, Inc.

Plasma and flow simulations have played vital roles to guide an advanced dielectric etch equipment design and process tuning to achieve desired process performance. Plasma simulation has been performed to study frequency effect on electron density, power deposition and dissociation fraction for a capacitively coupled discharge. Simulation results demonstrated that plasma generation efficiency enhances with increase in frequency while energy of the bombarding ions diminishes. A very high frequency source has been developed to generate high density plasma while RF bias has been used to control ion energy. Charge Species Tuning Unit (CSTU) tunes plasma density and ion flux distributions, and consequently the etch rate uniformity. Using flow simulation we evaluated species residence time that decides the extent of species dissociation in the process chamber. The gap between the showerhead and the wafer was optimized to achieve sufficient dissociation while minimizing the impact of flow convection on the wafer. Flow simulation also guided equipment design for high conductance over a large process window, and for azimuthal flow uniformity using a side pump. Using flow simulation we guided Neutral Species Tuning Unit (NSTU) design that can tune pressure and neutral flow distributions to the wafer, hence, CD bias and profile uniformities. The independent controls of plasma density and ion energy, and distributions of neutrals and ions played crucial roles in process development and tuning that are important for a production-worthy advanced dielectric etch equipment design and process tuning.

10:00am **PS+MS-ThM6 Effect of Reactor Geometry on Ion Energy Distributions for Pulsed Plasma Doping (P@super 2@LAD)@footnote 1@***, **A. Agarwal,*** University of Illinois at Urbana-Champaign*; M.J. Kushner,* Iowa State University

Ultra-shallow junctions (USJ) are required for fabrication of sub-0.1 µm transistors in semiconductor integrated circuits. Plasma implantation methods such as pulsed plasma doping (P@super 2@LAD) present simple, low cost alternatives to beam line technologies. P@super 2@LAD is capable of delivering high dose rates at ultra-low energies (0.02-20 keV) using conventional plasma processing technologies.@footnote 2@ In this talk, results from a computational investigation of P@super 2@LAD using different reactor geometries will be discussed. The investigation was performed using a modified version of the Hybrid Plasma Equipment Model to address quasi-dc pulsed biases.@footnote 3@ An inductively coupled plasma is used to generate ions in pressures of 10s mTorr. A quasi-dc pulsed bias is applied to the substrate to accelerate ions. Typical bias pulse lengths range between 5 and 50 µs and bias voltages are up to 20 kV. Results will be presented for Ar/NF@sub 3@ (a surrogate for Ar/BF@sub 3@) gas mixtures. The large bias voltages and long pulse lengths result in there being considerable thickening of the sheath during the pulse. Sufficient charge is extracted during the pulse that some amount of depletion of ions results. Non-uniformities in plasma density as the sheath extends into the plasma or the ability of the plasma to repopulate depleted charge can have a significant effect on the ion energy distributions (IEDs) to the substrate, which influences the doping profiles. For example, at sufficiently high biases (>2 kV), the IEDs can be skewed in the direction of the source of ion production with the result that the ions approach the substrate preferentially from one direction. As the sheath expands into the center of the reactor where the plasma density is higher, the rate of expansion slows. The result can be a laterally dependent sheath thickness which in turn affects the collisionality of ions crossing the sheath. The consequences of varying reactor aspect ratios and positioning of coils on IEDs will be discussed. @FootnoteText@ @footnote 1@ Work supported by VSEA, Inc. NSF (CTS03-15353) and SRC. @footnote 2@ S. B. Felch, B. -W. Koo, R. B. Liebert, S. R. Walther, and D. Hacker, Surf. Coatings Technol., 156, 229 (2002) @footnote 3@ A. Sankaran and M. J. Kushner, J. Vac. Sci. Technol. A, 22, 1242 (2004)

10:20am **PS+MS-ThM7 Computational Modeling of Process Induced Damage During Back End of Line Wafer Processing***, **S. Rauf,** M. Rasco, A. Haggag, R. Chatterjee, M. Moosa, K. Junker, P. Ventzek,* Freescale Semiconductor, Inc.

A variety of back end of line (BEOL) processes can subject ultra-thin gate dielectrics in transistors to extremely large electric fields or currents. These processes include plasma etching, plasma enhanced deposition and electron beam treatment of low-@kappa@ dielectrics. A computational modeling infrastructure is described in this presentation that is being used to address process induced damage issues for BEOL microelectronics manufacturing processes. The model couples simulations of plasma etching and electron beam processes to an electrostatic model for charging of gate dielectric. The 2-dimensional models for capacitively and inductively coupled etching plasmas are fluid-based and take account of the detailed plasma chemistry of etching plasmas. The electron beam process is simulated using a 1-dimensional Monte Carlo model. The 2/3 dimensional electrostatic model solves the coupled set of Poisson equation and current continuity equation. Dielectric and semi-conducting properties of materials are taken into account in the electrostatic model using nonlinear electric-field dependant conductivity. Computational results show that, if the gate dielectric is exposed to current from the processing equipment, it charges up rapidly leading to dielectric breakdown. The structure of the transistor, materials surrounding the transistors (e.g., insulation layers) and area of charge collection antennas determine how much current flows through the gate dielectric and the consequent damage that occurs to it. Examples are used to illustrate how this modeling infrastructure is being used to help design BEOL processes and integrations.

10:40am **PS+MS-ThM8 Computational Model for Ion Beam Extraction from a Pulsed Plasma Through a Grid***, **S.-K. Nam,** V.M. Donnelly, D.J. Economou,* University of Houston

A computational model was developed to study the energy and directionality of an ion beam extracted from a pulsed plasma through a grid. First, a fluid model was used to obtain the space and time resolved profiles (at the periodic steady state) of the active glow (power ON) of the 13.56 MHz plasma. Then, the plasma evolution in the afterglow (power OFF) was followed with the fluid model. A positive DC bias voltage (acceleration voltage) was applied at a specific time in the afterglow to raise the plasma potential and expel positive ions out of the plasma and through the grounded extraction grid. The electric potential profiles found by the fluid model were in turn used as a boundary condition in a Particle-in Cell (PIC) simulation of ion flow through the holes of the grid. The output of the PIC simulation was the energy and angular distributions of the extracted ion beam. Fractional beam neutralization by ion contact with the metal grid was also determined. Beam directionality improved by extracting ions in the afterglow as the electron temperature dropped precipitously. A smaller diameter of the grid holes and a greater DC acceleration voltage also improved beam directionality. The energy distribution of the beam was very sharp (assuming ideal step accelerating voltage) except at higher pressures when ion-neutral collisions played a role. Work supported by NSF-NIRT and the Texas Advanced Technology Program.

11:00am **PS+MS-ThM9 CKnudsen - a Chemkin-based Collisionless Transport and Surface Reaction Simulator***, **A.H. Labun,*** University of British Columbia - Okanagan, Canada

Reactive gas transport through a channel differs in the molecular flow (collisionless) regime from the flow in a fluid (collisional) regime. Chemical systems composed of gas and surface species and elementary reactions on the surface are simulated in the collisionless transport regime by CKnudsen, a new Chemkin code. Angular distributions for incident flux from all sources for each gas species are assembled at each point of the surface which encloses the volume. The system of simultaneous reaction rate equations is solved deterministically at each surface point. The reaction rates at each surface point together with the input angular flux distribution for each gas determine the angular distribution of reemitted flux for each gas. The use of the same Chemkin reaction formalism and subroutine libraries used by fluid codes facilitates multi-scale simulation and the validation of proposed reaction mechanisms in different regimes. As an example, Arora and Pollard's W CVD mechanism with 16 elementary surface reactions@footnote 1@ is converted into Chemkin format and evaluated at the equipment scale and then at the feature scale in submicron trenches and compared to experimental results. @FootnoteText@ @footnote 1@ R. Arora and R. Pollard, J. Electrochem. Soc. vol. 138, 1523-1537 (1991).

11:20am **PS+MS-ThM10 Simplified Model for the DC Planar Magnetron Discharge***, **G. Buyle**, D. Depla, R. De Gryse,* Ghent University, Belgium

In order to investigate the DC planar magnetron discharge, we developed a simplified 2D model.@footnote 1@ This model differentiates itself from numerical models by analytically calculating the ionization caused by the high energy electrons, i.e. the electrons with energy above the ionization threshold. The model also takes into account that secondary electrons, which are emitted from the target due to ion bombardment, can be recaptured by the target.@footnote 2@ Here, the simplified model is extended such that the discharge current can be calculated. To achieve this extension, the Child-Langmuir law is applied and adapted to account for the specific magnetron discharge conditions. This way, a self-consistent model for the magnetron discharge is obtained. The extended simplified model allows investigating the influence of different external parameters on the magnetron discharge. The parameters considered are the magnetic field strength, the gas pressure, the secondary electron yield and the electron reflection coefficient. The latter two parameters are mainly determined by the target material. Special attention is given to the influence of these parameters on the current-voltage characteristic. Especially the considered target material properties seem to have a strong influence: increasing the secondary electron yield shifts the current-voltage characteristic to lower discharge voltages and increases its slope. Increasing the electron reflection coefficient leads to the same changes but their magnitude is larger. @FootnoteText@ @footnote 1@ G. Buyle et al., Vacuum 74 (3-4), 353-358, 2003.@footnote 2@ G. Buyle et al., J. Phys. D: Appl. Phys. 37, 1639-1647, 2004.

Plasma Science and Technology
Room 304 - Session PS-ThM

Plasma-Surface Interactions II

Moderator: W.M.M. Kessels, Eindhoven University of Technology, the Netherlands

8:20am **PS-ThM1 Plasma-Based Techniques to Reduce/Remove Particle Contamination for Pelicleless EUV and Imprint Lithography***, **D.N. Ruzic**, D.A. Alman, B.E. Jurczyk, H. Qiu, M.J. Neumann,* University of Illinois at Urbana-Champaign

Particle contamination on EUV surfaces during mask blank deposition, mask fabrication, patterned mask handling can create significant distortions and loss of reflectivity and must be avoided. Particles on the order of 10nm are problematic during MLM mirror fabrication, since the introduced defects disrupt the local Bragg planes. The most serious problem is the accumulation of particles on surfaces of patterned blanks during EUV light exposure, since >25nm particles will be printed without an out-of-focus pellicle. Particle contaminants are also a problem with direct imprint processes since defects are printed every time. Several plasma-based techniques are under investigation aiming to reduce particle contamination through the use of controlled electrostatic repulsion and expulsion of particles from surfaces. The preliminary experiment simulates the particle contamination of mirror samples by introducing external insulating nano-particles of 85% of particles. Particles are imaged with a high-resolution SEM and numerically counted using contrast information from the image histogram. The capabilities for extending this process to higher levels suitable for manufacturing will be discussed.

8:40am **PS-ThM2 Plasma-Surface Reactions at a Spinning Wall***, P.F. Kurunczi, J. Guha, **V.M. Donnelly**,* University of Houston

We report a new method for studying plasma-wall interactions in near-real time. A cylindrical substrate is embedded in the reactor wall. This "spinning wall" is rotated up to 200,000 rpm, allowing the surface to be periodically exposed to the plasma (40% of the time) and then analyzed by a chopped molecular beam mass spectrometer (MS) in as little as 150µs after plasma exposure. Skimmers on the plasma side and analysis side of the spinning wall, and 3 stages of differential pumping allow a pressure of 10@super -10@ Torr in the MS with a 10 mTorr plasma. We have used this method to study oxygen plasma reactions on anodized Al. With the plasma off and substrate at rest, we observe a small signal at m/e = 32, due to O@sub 2@. When the substrate is rotated (plasma off) this signal increases slightly. When the substrate is at rest and the plasma is turned on, no increase in signal is observed. When the substrate is spun with the plasma on, however, a large increase in signal is observed with increasing rotation frequency. We interpret these observations as follows: O-atoms that impinge on the surface when it is in the plasma recombine over the ~0.7 to 30 ms period probed by changing the rotation frequency. We rule out O@sub 3@ (cracking in the MS ionizer to form O@sub 2@) from the absence of its parent ion. Likewise, we rule out shallow implantation of O@sub 2@@super +@ or O@super +@ as a cause of the O@sub 2@ signal; the dependence of the signal on rotation frequency did not change when grids were positively biased to reject positive ions. No desorbing O was observed; a signal at m/e=16 was entirely from the cracking of O@sub 2@. Finally, no ions were observed with the MS ionizer off. Modeling of O@sub 2@ signal vs. rotation frequency indicates a range of recombination rate constants, suggesting a range of O-binding energies on anodized Al. Supported by ACS-PRF. @FootnoteText@ P.F. Kurunczi - Present affiliation: Varian Semiconductor Equipment, Gloucester, MA 01930.

9:00am **PS-ThM3 Innovative Strategy to Improve the Stability of Plasma Processes***, **R. Ramos**, G. Cunge, B. Pelissier, O. Joubert,* CNRS/LTM, France

Plasma process drifts associated with changes in the reactor wall conditions have become a major issue in silicon etching processes used in integrated circuit fabrication. The solution today to achieve good wafer-to-wafer repeatability is the dry-cleaning of the chamber in fluorine-based plasma between each wafer. However, this procedure leaves AlF residues on the Al@sub 2@O@sub 3@ reactor walls. This leads to several issues including flake off of AlF@sub x@ particles on the wafer and process drifts - due both to the progressive growth of AlF material and to the release of F atoms from the chamber walls during the etching process. For all these reasons, we are introducing here a new strategy to improve the stability of plasma processes. Before the etching process, a thin carbon-rich layer is deposited on the reactor walls by a short plasma step. After silicon gate etching, the SiOCl layer formed on the carbon layer is cleared with an appropriate plasma chemistry and the carbon layer removed by an O@sub 2@ plasma, thus resetting the reactor walls to their initial state. Using this strategy the process is perfectly reproducible since it always starts under the same carbon-rich chamber walls conditions. At the same time, issues associated with AlF deposits are prevented because chamber walls are protected from aggressive fluorine-based cleaning plasma. X-ray Photoelectron Spectroscopy analysis of the reactor wall surfaces is used to show feasibility and efficiency of this technique in an industrial context. Then performance of state-of-the-art silicon gate etching process in carbon-coated chamber and in traditionally seasoned chamber are compared in terms of feature profile, etch rate and selectivity toward gate oxide. Correlation with time-resolved broad-band UV absorption spectroscopy analysis of plasma gaseous phase suggests promising future of this strategy for metal gate etching.

9:20am **PS-ThM4 Interactions of Plasmas with Model Polymers for Advanced Photoresists***, **S. Engelmann**, X. Hua, T. Kwon, R. Phaneuf, G.S. Oehrlein,* University of Maryland*; Y.C. Bae,* Rohm and Haas Electronic Materials*; D.B. Graves, E. Paragon,* University of California, Berkeley*; E.A. Hudson,* Lam Research Corp.*; P. Lazzeri, E. Iacob, M. Anderle,* ITC-Irst, Italy

Plasma-based pattern transfer of lithographically produced nanoscale patterns in advanced resist materials is often accompanied by resist surface roughening and line edge roughening. The properties of the organic imaging materials or fully formulated resist systems as well as the reactive particle fluxes and microscopic parameters of the plasma processing environment contribute to these changes. In this collaboration, we seek to establish a basic understanding of these phenomena by investigating the interaction of a number of carefully selected model polymers like those used in advanced photoresist materials, along with fully formulated 193nm and 248 nm photoresist systems, with well characterized plasmas. We have systematically studied the evolution of surface roughening and surface composition in these systems using H@sub 2@, O@sub 2@, C@sub 4@F@sub 8@/Ar and Ar discharges produced in an inductively coupled plasma (ICP) reactor. Etching rate, surface composition and chemical structure was evaluated using Ellipsometry, Atomic Force Microscopy, Fourier-Transform Infrared Spectroscopy, Static Time-of-Flight Secondary Ion Mass Spectrometry and X-Ray Photoelectron Spectroscopy. The exposed compounds showed different chemical evolutions for various plasma exposures. We will discuss these differences with regard to the chemical structure of the different monomers used in the model compounds.

9:40am **PS-ThM5 Decomposition Mechanisms of 193 nm Photoresist under Ar+ and Radical Bombardment***, **E. Pargon**, D. Nest, D.B. Graves,* University of California at Berkeley*; G.S. Oehrlien, S. Engelmann, X. Hua,* University of Maryland*; Y.C. Bae,* Rohm and Haas Electronic Materials, L.L.C.*; E.A. Hudson,* Lam Research Corporation

193 nm methacrylate-based photoresists are known for their limited etch resistance and enhanced surface roughening compared to 248 nm photoresist. In this study, we examine the decomposition mechanisms of three 193 nm methacrylate-based photoresist formulations in a vacuum beam experiment. The vacuum beam system allows separate control of incident ionic and neutral radical species, more controlled exposure protocols and direct detection of etch products. The results obtained in the beam experiment are compared to complementary and analogous measurements made in a plasma etch environment. Photoresist samples are exposed to an Ar+ ion beam (100 eV - 1000 eV) and various radical beams. The species leaving the surface are detected in an in-situ threshold ionization quadrupole mass spectrometer. Film thickness and mass change are monitored during and after beam exposure. FTIR is used in transmission mode to detect changes in film structure after beam exposure. The primary volatile species leaving the room temperature photoresist surface during Ar+ ion bombardment are CO and H2O, with significant quantities of CO2 and C2H2 also detected. Volatile species initially leave the surface at a higher rate, and the initial etch rate is significantly higher than the average etch rate. FTIR measurements after beam exposure show that the most significant changes occur in the CH2 and CH3 stretching modes (3000 cm-1), although other changes in the carbonyl region (1700 cm-1) are observed as well. We report the effects of beam exposure on surface roughness as measured by ex-situ AFM. The impact of surface temperature and various radical fluxes (H, N and O) on decomposition rate and product distribution will also be reported.

10:00am **PS-ThM6 Investigation of Feature Surface Roughening using Plasma Beams***, **Y. Yin**, H.H. Sawin,* MIT

Plasma etching processes often roughen the feature sidewalls, leading to the formation of anisotropic striations. The primary cause of sidewall roughening is the templating of mask roughness into the underlying film. Specifically, the inherent roughening of photoresist provides the mask for templating effect. To fully understand the sidewall roughness evolution, it is critical to characterize the inherent roughening of photoresist as well as other materials, such as porous low-k film. A polymerization-induced micromasking mechanism was proposed to explain the surface roughening of porous low-k films. Porous structure in the substrate plays a critical role in the film roughening evolution. This effect can be understood using the concept of pore filling with polymeric deposition that etches more slowly under fluorocarbon plasma exposure. Later on, the polymer forms micromasks that induce roughening. Although scaled with the ion bombardment energy, the roughness level of porous low-k film etched in C2F6 plasma is mainly related to the film thickness removed; no similar trend was observed on non-porous OSG films under same etching conditions. Fluorocarbon plasmas with different polymerization capabilities such as 20% C4F8/ 80% Ar, were used to explore the polymerization effects. Additionally, the correlation between polymer deposition and porosity/pore size distribution of low-k films was investigated. The roughening of photoresist blank films can also be explained based upon the mechanism proposed above. It was found that photoresist roughening was influenced by etching chemistries and some other factors. In particular, the inhomogeneity introduced during blank film development process formed some equivalent "pores" at near surface region. These "pores" had significant impact on the roughness evolution during etching in fluorocarbon plasmas.

10:20am **PS-ThM7 3-Dimensional Feature Scale Profile Simulation of Sidewall Roughening During Plasma Etching***, **H. Kawai**, B. Bai, H.H. Sawin,* Massachusetts Institute of Technology

Sidewall roughness or Line Edge Roughening (LER) is becoming an ever more significant issue as the line width of integrated circuits features shrink and the size of width variation caused by LER becomes comparable to the minimum feature dimension. Since roughening is inherently a three dimensional phenomenon, we have developed a 3-dimensional feature scale profile simulator to simulate the surface and sidewall roughening during the etching process of polysilicon and silicon dioxide. The simulator uses a dynamic Monte Carlo simulation to model the surface kinetics. The simulation domain is discretized into array of cubic cells with the side of 2.5 nm. The local surface conformation is determined by fitting the local region of the surface cells with a polynomial, which is used to compute the surface normal, scattering angle, and flux on the 3-D surface. Using the angular dependence of physical sputtering with a highest etching yield at 60 degrees off-normal incident angle, the initially smooth polysilicon surface is roughened with facets of approximately 60 degrees after the surface is sputter-etched at normal incident angle. Non-planar surfaces are etched and evolve to the same surface roughness as was found for the initially planar surface. However, using the angular dependence of ion (chlorine) etching yields where yield decreases monotonically with off-normal angle, an initially smooth polysilicon surface tends to stay smooth after it is etched at normal incident angle. The surface with small, shallow angle initial roughness also smoothes when it is etched at glancing incident angle, but the surface with large, steep features forms striations after it is etched due to the scattering of ions. Templating, also known as top LER, the most common mechanism of LER caused by mask edge roughening, has also been modeled. This LER is characterized by the transference of the mask spatial frequencies with reduced amplitude with distance from the mask.

10:40am **PS-ThM8 Surface Modification of Photoresists in Electron Beam-Generated Plasma***, **B. Orf**, G.S. Oehrlein,* University of Maryland at College Park*; D. Leonhardt, S.G. Walton,* US Naval Research Laboratory

An electron beam (e-beam) generated plasma system has been used to study the factors that contribute to plasma-induced surface modifications of UV photoresists. Due to the low electron temperature of e-beam generated plasmas, minimum ion energies are much lower than in RF excited plasma discharges, and can be more accurately controlled in the low energy regime. Thus surface modifications such as roughening, compositional changes, and bond rearrangements (i.e. cross-linking, graphitization) can be studied systemically with respect to the ion energy. In this work we have examined the interaction of Ar and Ar/fluorine plasmas with commercial 193 nm and 248 nm photoresists. Following plasma exposure, the photoresist films were characterized ex situ by X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), contact angle measurements and ellipsometry. Ion energy and exposure time were carefully selected to establish the role of ion bombardment in the surface modification, and determining the threshold energies for photoresist damage versus etching. Additionally, the effect of surface relaxation time was investigated by modulating the e-beam generated plasma, to understand how long-lived radicals and the organic material react during the plasma afterglow. The observed differences in behavior of the 193 nm and 248 nm photoresists will be discussed in terms of compositional and structural differences of the materials.

11:00am **PS-ThM9 Nanoscale Plasma Processing of Substrates Using Moving Patterned Shutter***, **X. Hua**, G.S. Oehrlein,* University of Maryland*; P. Lazzeri, M. Anderle,* ITC-irst, Italy

Future nanoscale device fabrication may require the ability to add or remove controllably layers of several nanometers using plasma processes. For such processes, the total length of the substrate-plasma interaction time decreases to a few seconds and less. For short plasma-substrate interaction times, transient plasma effects, e.g. electrical matching and plasma stabilization, plasma-wall interactions, etc., play a more important role than for longer plasma processes, and reduce our ability to control the plasma induced modification of a substrate. In this presentation, we describe the concept of a moving shutter containing slits in close contact with a substrate to control the interaction time of well-established gas discharges with the substrate for nanoscale layer/nanostructure processing. Both substrate and shutter are located on the RF powered electrode and can be biased relative to the plasma. Once the plasma density, discharge chemistry, and the electrode bias voltage are fully established, the shutter with slits begins to move at a controlled speed across the initially covered substrate and exposes the substrate for the desired interaction time to the plasma. We will show that this technique enables precise nanoscale layer etching or deposition on both blanket and patterned substrates employing gas discharges. Applications of this approach to nanoscale plasma processing of ultra low k materials and surface modifications of advanced photoresist materials are reviewed.

11:20am **PS-ThM10 Investigation of the Etching Characteristics of SrTiO@sub 3@ Films in Halogenated High-Density Plasmas*, L. Stafford*[1]*,* *O. Langlois,* Universite de Montreal, Canada*; M. Gaidi,* INRS-Energie, Materiaux et Telecommunications, Canada*; J. Margot,* Universite de Montreal, Canada*; M. Chaker,* INRS-Energie, Materiaux et Telecommunications, Canada*; J. Saussac,* Universite de Montreal, Canada

SrTiO@sub 3@ (STO) films have recently received much attention because of their potential applications into waveguides for optical integrated systems. Up till now, relevant issues related to the development of an efficient patterning process for STO remain however to be solved. This is vital since the performances of the device critically depend upon the STO etching characteristics, particularly upon the roughness of the etched profiles. In this context, we investigate in this work the etching characteristics of STO films using a low-pressure high-density plasma operated in halogenated gas mixtures. We found that the addition of Cl@sub 2@ and SF@sub 6@ to the Ar plasma significantly reduces the etch rate. A correlation between the etch rate data and the plasma characteristics obtained from Langmuir probes and actinometry, indicates that this decrease results in part from the lower positive ion density in Ar/Cl@sub 2@ and Ar/SF@sub 6@ plasmas. Using a recently developed surface reaction model for ion-assisted chemical etching,@footnote 1@ we demonstrate that in both Ar/Cl@sub 2@ and Ar/SF@sub 6@ plasmas, (i) the etch rate is ion-flux limited (i.e. independent of the reactive neutral density) and that (ii) chlorine and fluorine reactive neutral species act as inhibitors in the etching process of STO. A characterization of the post-etched surface by X-Ray Photoelectron Spectroscopy (XRPS) and Secondary Ion Mass Spectrometry (SIMS) measurements indicates that inhibition results from the formation of a thin SrCl@sub x@ or SrF@sub x@ layer, which impedes the formation and/or the desorption of TiCl@sub x@ or TiF@sub x@ volatile products. Finally, based on XRPS and SIMS measurements, we propose a two-layer model for the representation of the surface in the course of etching. @FootnoteText@ @footnote 1@ L. Stafford, J. Margot, M. Chaker, & S.J. Pearton, "Energy dependence of ion-assisted chemical etch rates in reactive plasmas", submitted to Appl. Phys. Lett. 21/12/2004.

11:40am **PS-ThM11 A Numerical Model for Profile Anomalies Caused by Surface Charging during Etching and Overetching of Polysilicon*, Y. Osano,*** *K. Ono,* Kyoto University, Japan

The precise control of etched profiles in gate etch processes is one of the most important issues. However, the mechanism of etching processes is not fully understood; in particular, the particle transport and reaction processes in microstructures are considerably difficult to be understood, owing to a number of physical and chemical effects. Among these effects, the surface charging on insulating masks during etching causes the deflection of ion and electron trajectories in microstructures. Moreover, the charging on electrically floating poly-Si on SiO@sub 2@ films during overetching step causes a significant deflection of ion trajectories in microstructures. It is generally appreciated that the deflection of ion trajectories leads to the nonuniformity of ion fluxes onto the feature surfaces, which in turn results in profile anomalies such as bowing, microtrenching, and notching. In this paper, we present a phenomenological, pseudo atomic scale model to simulate the feature profile evolution of Si etching in Cl@sub 2@. The model incorporates the surface charging in microstructures, to investigate its influence on the profile evolution. The particle transport of Cl@super +@ ions, Cl neutrals, and electrons in microstructures onto etched substrates is analyzed by the Monte Carlo calculation. The model gives the electrostatic potential distribution, along with the differential charging that occurs on insulating masks, electrically floating Si, and SiO@sub 2@ films. The flux of ions and electrons onto feature surfaces is self-consistently analyzed by taking into account their deflection due to Coulomb interaction with charged feature surfaces. The feature profile evolution is presented by the cell removal method. The numerical simulation is performed with different incident ion energies and pattern widths. Emphasis is placed on the mechanism for the formation of microtrenching and notching, which are generally considered to be mainly caused by the surface charging.

Surface Science
Room 200 - Session SS1-ThM
Water-Surface Interactions

Moderator: B.D. Kay, Pacific Northwest National Laboratory

8:20am **SS1-ThM1 Metal/Electrolyte Interfaces: In-situ Scanning Tunneling Microscopy Studies*, K. Wandelt,*** University of Bonn, Germany **INVITED**

In the years to come more and more processes at solid/liquid interfaces will replace processes which nowadays are carried out by vacuum based methods, like surface modification, thin film growth, nanostructuring, etc.. Among others this is a consequence of the growing number of methods which are capable to provide in-situ information about properties and processes at solid/liquid interfaces with the same precision as we are used to in vacuum. This is particularly true for ElectroChemical Scanning Tunneling Microscopy (ECSTM), which - in combination with in-situ FTIR- and some ex-situ spectroscopies - is used in this work to characterize copper single crystal electrodes interacting with various electrolytes. Firstly, surface structural phase transitions and morphological changes due to the adsorption of simple anions, like Cl, Br, J, S, SO@sub 4@, SCN, etc., will be studied with atomic resolution. Secondly, it will be shown that the halogen and sulphur covered electrode surfaces are interesting primary templates for the formation of thin ordered compound films (e.g. CdCl@sub 2@)) as well as self-assembled organic nanostructures (e.g. from porphyrins and viologenes). In particular the latter ones are found to form chiral cavitands, which in turn are ideal secondary templates for the design of more complex molecular architectures with nanoscale periodicity and specific functionality.

9:00am **SS1-ThM3 Segregation of Anions at the Alkali Halide Solution/Vapor Interface Investigated by Photoemission Spectroscopy***, S. Ghosal,* University of California, Irvine*; **H. Bluhm,*** Lawrence Berkeley National Laboratory*; B.S. Mun,* Lawrence Berkeley National Laboratory, US*; G. Ketteler, F.G. Requejo, E.L.D. Hebenstreit, D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory*; J.C. Hemminger,* University of California, Irvine

Ion-enhanced interactions with gases at aqueous solution interfaces may play an important role in the chemistry of concentrated inorganic solutions in the atmosphere. Using ambient pressure photoemission spectroscopy (PES) we have measured the concentration of ions at the surface of saturated potassium iodide and potassium bromide solutions. In the case of saturated potassium iodide solutions two iodine 4d peaks that are separated by a binding energy difference of 1.7 eV can be identified in the PES spectrum. Using photon-energy-dependent depth-profiling we have determined that the iodine peak with the higher binding energy is due to an iodine species at the solution interface, while the low binding energy peak is due to iodine from the bulk of the solution. The presence of an anion species at the solution interface is in agreement with our previous ambient pressure PES results that showed an enhancement of the halide anion concentration at the solution interface compared to the literature value for bulk solutions.@footnote 1@ @FootnoteText@ @footnote 1@S. Ghosal at al., Science 307, 563 (2005).

9:20am **SS1-ThM4 The Growth of Thin Water Films on a Hydrophobic Water Monolayer on Pt(111)*, G.A. Kimmel,*** *N.G. Petrik, Z. Dohnalek, B.D. Kay,* Pacific Northwest National Laboratory

The growth of amorphous solid water and crystalline ice films on Pt(111) is investigated using rare gas physisorption. For a wide range of growth temperatures (20 - 155 K), the water monolayer wets the Pt(111). However, crystalline ice films grown on the water monolayer do not wet that surface. In contrast, amorphous films grow layer-by-layer for at least the first three layers over a wide range of growth temperatures (20-120 K), probably due to kinetic limitations. Wetting films grown at low temperature that are subsequently annealed to high temperature typically unwet during or after the crystallization of the films. The results are surprising since it is commonly believed that water films wet Pt(111). However, they are consistent with recent theory and experiments suggesting that the molecules in the water monolayer are fully coordinated forming a hydrophobic surface with no dangling OH bonds or lone pair electrons and a low surface energy.

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[1] **PSTD Coburn-Winters Student Award Finalist**

9:40am **SS1-ThM5 The Nature of Water on Oxygen Covered Pt: Low Temperature Activation and Unexpected Structure***, **T. Schiros**, H. Ogasawara,* Stanford Synchrotron Radiation Laboratory*; L.-Å. Näslund, M. Odelius, L.G.M. Pettersson,* Stockholm University, Sweden*; A. Nilsson,* Stanford Synchrotron Radiation Laboratory

The nature of the adsorbed water layer on surfaces has been a topic of interest due to its relevance for many practical fields, including corrosion, electrochemistry, environmental science and heterogeneous catalysis. Recently the behavior of adsorbed water under the presence of oxygen has garnered increasing interest in connection to the triple phase boundaries problem in fuel cell catalysis. Here, we studied the co-adsorption of water and oxygen on Pt(111) with X-ray photoemission and X-ray absorption spectroscopy in an ultra high vacuum environment combined with electronic structure calculations in the frame work of density functional theory. While water absorbs intact on clean metal surfaces at low temperature,@footnote 1-3@ an oxidized Pt surface activates and splits adsorbed water even at low temperature. We propose a new structure model for the activated water on Pt(111). We find that the activated water aligns the molecular axis perpendicular to the surface and is hydrated in the equatorial plane. @FootnoteText@ @footnote 1@ H. Ogasawara et al, Phys. Rev. Lett. 89 (2002) 276102.@footnote 2@ K. Andersson et al, Phys. Rev. Lett. 93 (2004) 196101.@footnote 3@ K. Andersson et al, Surf. Sci. Lett. In press (2005). .

10:00am **SS1-ThM6 DFT Calculations of Interaction of Water Molecules with Pt(111) Surface***, **L. Árnadóttir**,* University of Washington*; H. Jónsson,* University of Iceland*; E.M. Stuve,* University of Washington

The interaction of water molecules with the Pt(111) surface has been studied using DFT and the PW91 functional. Early stages of ice crystal nucleation and the possibility of dissociation on flat terrace, kink and steps have in particular been addressed. In the lowest energy configuration, a water molecule sits on top of a Pt atom and donates an electron pair into an empty d-orbital on the Pt. The binding energy is found to be 0.30 eV. Small water clusters of two and three water molecules also have lowest energy configuration on top of a Pt atom. In those small clusters one water molecule is centered on the top of a Pt surface atom and is tilted with the hydrogen atoms pointing about 16° away from the surface plane and the other water molecules about 0.5 Å further away from the surface. While the dissociation of water molecules is uphill by 0.72 eV on the flat terrace, it is almost neutral energetically at the step but has an activation energy of 0.91 eV. The dissociation will, however, not occur thermally because desorption will occur more readily. As the temperature is raised, the diffusion of single water molecule is predicted to become active on the time scale of seconds at a temperature of 43 K which is in good agreement with recent experimental results of Kay and coworkers.@footnote 1@. The binding at steps and kinks on the Pt(111) surface is substantially stronger than at the flat terrace, by 0.16 eV and 0.25 eV, respectively, and the lowest energy configuration has the water molecule sitting on top of edge or kink atoms. At low coverage, clusters of water molecules would, therefore, be expected to line the upper side of step edges. This is consistent with experimental STM images taken by Morgenstern et al.@footnote 2@ @FootnoteText@@footnote 1@ Daschbach, J. L., Peden, B. M., Smith, R. S., Kay, B. D.,J. Chem. Phys., 2004. 120(3): p. 1516-1523 @footnote 2@ Morgenstern, M., Michely, T., Comsa, G., Phys. Rev. Lett., 1996. 77(4): p. 703-706

10:20am **SS1-ThM7 The Effect of Incident Collision Energy on the Phase, Crystallization Kinetics, and Porosity of Vapor Deposited Amorphous Solid Water Films***, **T. Zubkov**, R.S. Smith, Z. Dohnálek, B.D. Kay,* Pacific Northwest National Laboratory

Molecular beam techniques that allow for the precise control of the impingement flux, deposition angle, and incident collision energy are used to grow nanoscale films of amorphous solid water (ASW). The phase (amorphous or crystalline), porosity, and subsequent crystallization kinetics of the ASW films are probed using temperature programmed desorption, inert gas physisoption, and infrared spectroscopy. We find that for films grown at 20 K and normal incidence, the incident collision energy (up to 2 eV) has no effect on the phase of the deposited film or the subsequent crystallization kinetics. On the other hand, the incident beam energy does affect the porosity of the deposited films. At low beam energy (0.05 eV), the porosity of the vapor deposited film depends strongly on the incident growth angle. Films with structures from non-porous to highly porous can be grown by increasing the angle of incidence of the impinging molecules. The porosity of the ASW films decrease with increasing beam energy. The results of these experiments and their implications for the physical properties of ASW are presented and discussed. Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy.

10:40am **SS1-ThM8 Ionization of Water-Ice Layers on Platinum: Effect of Carbon Monoxide***, **R.A. Manghani**, V.K. Medvedev, E.M. Stuve,* University of Washington

Field ionization of water on a platinum field emission tip was studied in the presence of carbon monoxide (CO) as co-adsorbate. Water adlayers 5 - 400 Å thick were grown under field-free conditions at 108 K by exposure of cryogenically cooled emitter tip to water vapor in ultrahigh vacuum. Onset of field ionization of water layers was probed by ramped field desorption (RFD) on platinum and CO saturated platinum emission tip. Onset field for water ionization on CO saturated platinum was found to be lower than that for water adsorbed on bare platinum. Facilitation of ionization by saturated CO on platinum was attributed to enhancement in the local field. The effect decreased with increasing water thickness, but existed for thick water layers. Effect of CO on water ionization is discussed and a model is presented.

11:00am **SS1-ThM9 Electron-Stimulated Production of Molecular Oxygen in Thin Films of Amorphous Solid Water on Pt(111)***, **N.G. Petrik**,* Pacific Northwest National Laboratory*; A.G. Kavetsky,* Khlopin Radium Institute, Russia*; G.A. Kimmel,* Pacific Northwest National Laboratory

The electron-stimulated reactions in amorphous solid water (ASW) films leading to the production of molecular oxygen were investigated. Thin (0-400 ML) amorphous films of H@sub 2@@super 16@O, H@sub 2@@super 18@O, and D@sub 2@O deposited on Pt(111) were irradiated with 87 eV electrons, and the electron-stimulated desorption (ESD) of O@sub 2@ was measured versus film thickness and isotopic composition. The O@sub 2@ ESD yield is low for small coverages, has a maximum at ~20 ML, and decreases to a coverage independent level for coverages greater than ~50 ML. The O@sub 2@ and H@sub 2@ ESD yields versus ASW coverage are similar, indicating that both originate from mobile electronic excitations produced in the bulk of the ASW film that subsequently diffuse to the ASW/Pt and ASW/vacuum interfaces where they induce reactions. However in contrast to H@sub 2@, experiments with layered films of H@sub 2@@super 16@O and H@sub 2@@super 18@O show that O@sub 2@ is produced only near the ASW/vacuum interface. The O@sub 2@ molecule is produced via a relatively fast radiation-induced process from a stable precursor, perhaps HO@sub 2@ or H@sub 2@O@sub 2@, which accumulates at the ASW/vacuum interface. The results suggest that mobile electronic excitations produce a reactive species at the ASW/Pt interface, such as OH, which subsequently diffuses through the film to the ASW/vacuum interface where further reactions produce the stable precursors for the O@sub 2@ molecules.

11:20am **SS1-ThM10 A Comparison of H@sub 2@O and D@sub 2@O Adsorption on MgO(100) Under Ambient Conditions***, **M.C. Foster**, N.J. Ward, D. Passno,* University of Massachusetts - Boston

Transmission Fourier transform infrared spectroscopy is used to investigate both H@sub 2@O and D@sub 2@O adsorbed on the (100) face of MgO under ambient conditions. A sample cell has been constructed such that many of these infrared transparent surfaces are investigated while the volume of gas phase molecules probed is minimized. A number of crystals, obtained by cleaving with a hammer and chisel a larger single crystal boule under a nitrogen purge, are placed in this cell, which is essentially a hollow stainless steel tube with IR windows on either side. Water is introduced at the desired pressure and allowed to establish a dynamic equilibrium with the MgO(100). The adlayer formed on the crystal faces is observed by transmission Fourier transform infrared (FTIR) spectroscopy. Any IR absorption stemming from molecules in the gas phase in the resulting spectrum is easily subtracted out. From these measurements, we find that water reversibly adsorbs to MgO(100) creating liquid-like layers at room temperature with slight hysteresis seen during a complete adsorption / desorption cycle. The adsorption isotherm of water on MgO(100) resembles a typical BET plot, which coupled with by the fact that IR absorption due to either the OH or OD stretch of the adsorbed water does not change as a function of coverage, suggests that the layer grows in via three-dimensional island formation. Special attention has been paid to the issue of dissociative adsorption of water on the surface, either reversible or permanent with no evidence seen under these experimental conditions.

11:40am **SS1-ThM11 Water Adsorption on a Polymer Surface*, L.G. Rosa*[1]**, University of Nebraska-Lincoln*; Ya.B. Losovyj,* Louisiana State University*; I.N. Yakovkin,* Institute of Physics of National Academy of Sciences of Ukraine*; P.A. Dowben,* University of Nebraska-Lincoln, US

Water absorption and adsorption on the thin films of the ferroelectric copolymer polyvinylidene fluoride with 30% trifluoroethylene, P(VDF-TrFE,70:30) has been explored by angle resolved thermal desorption, angle resolved photoemission spectroscopy, high resolution photoemission spectroscopy and x-ray diffraction. We observe that water is absorbed into the polymer bulk. When the near surface region is saturated, an ice layer at the surface of the polymer can be formed. Strong dipole - dipole interactions between the dipole of water and the dipole of the ferroelectric polymer play an important role in absorption and desorption, including but not limited to, isotopic exchange and dielectric properties. Adsorbed water seems to be a spectator to the many phase transition of the ferroelectric polymer particularly the ones at the surface and bulk.

Surface Science
Room 202 - Session SS2-ThM
Functionalization of Semiconductor Surfaces

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

8:20am **SS2-ThM1 Dissociative Chemisorption of SiH@sub 4@ on Si(100): Threshold Energy and Mechanism*, H.L. Abbott*[2]**, University of Virginia*; D.F. Kavulak,* University of California, Berkeley*; I. Harrison,* University of Virginia

A three-parameter local hot spot model of gas-surface reactivity is employed to analyze and predict dissociative sticking coefficients for SiH@sub 4@ incident on Si(100) under varied nonequilibrium conditions. Two Si surface oscillators and the molecular vibrations, rotations, and translational energy directed along the local surface normal are active degrees of freedom in the 15 dimensional microcanonical kinetics. The threshold energy for SiH@sub 4@ dissociative chemisorption is found to be 19 kJ/mol, in quantitative agreement with recent GGA-DFT calculations that predict an intra-dimer mechanism. A simple scheme for increasing the rate of chemical vapor deposition of silicon from SiH@sub 4@ at low surface temperatures and/or on hydrogen passivated Si(100) is discussed.

8:40am **SS2-ThM2 Organic Functionalization of Semiconductors Using Amino Acids; Quantum Resonance Coupling and Electron Transport Effects***, G.D. Guilluame, G. Zhang,* ***C.B. Musgrave***, Stanford University

We have used DFT to simulate the attachment of amino acids and various unique organic molecules on Si and Ge surfaces. These structures have potential applications in molecular electronics and sensors if their structures can be controlled and if the resulting interface electronic structure provides appropriate electronic properties. We will present a summary of the various unique reactions of amino acids on Si(100)-2x1 we have investigated and focus on certain organics functionalities that are stabilized on Si and Ge by quantum mechanical resonance which stabilize the product and leads to stronger electronic coupling between the attached organic and the semiconductor substrate which might be useful in improving electrode-molecule charge transfer for organic-semiconductor molecular electronic devices. We will also discuss the accurate simulation of the electronic band structure of these molecular junctions required for correct prediction of the electron transport across these junctions. We have found that the common DFT methods are inadequate for this task, although the KMLYP method correctly predicts the HOMO and time-dependent KMLYP (TD-KMLYP) correctly predicts the LUMO energy.

9:00am **SS2-ThM3 Amide Chemistry at the Ge(100)-2x1 Interface*, A.J. Keung*,** *M.A. Filler,* Stanford University*; S.F. Bent,* Stanford University, US

Organic functionalization of semiconductor surfaces has many potential applications including semiconductor processing, molecular electronics, and chemical sensors. In particular, understanding the surface reactivity of the amide linkage could be important in developing biologically-based devices. In situ vibrational spectra were obtained as a function of coverage, temperature, and time for a series of primary, secondary, and tertiary amides absorbed on the Ge(100)-2x1 surface under ultrahigh vacuum conditions. For the tertiary amides, including dimethyl formamide, 1-methyl-2-pyrrolidinone, and n,n-dimethyl acetamide, asymmetric and symmetric N-C-O stretching, aldehydic C-H bending, as well as methyl deformation modes were observed, while Ge-H stretching modes were absent. This data provides evidence that tertiary amides form a dative-bond between the carbonyl oxygen and the electrophilic germanium dimer atom. Theoretical spectra of dative-bonded structures, calculated with density functional theory, agree well with experiment. In addition, these products desorbed at 310K on the timescale of minutes suggesting dative-bonded tertiary amides are just at the cusp of stability on Ge(100)-2x1. The primary and secondary amides, formamide and n-methyl formamide, respectively, were also investigated. Two types of products were observed for each compound at room temperature. Comparison to the experimental spectra of dimethyl formamide provides evidence for dative-bonded products. Dissociation products were also formed as evidenced by the growth of Ge-H stretches. The dissociation products were favored at higher temperatures, and there is evidence for dative-bonded adducts converting to these products upon annealing. Due to a kinetic barrier to this reaction, the dative-bonded state can be isolated at low temperature. These results have implications for understanding the reactivity of larger biological molecules such as peptides.

9:20am **SS2-ThM4 Layer-by-Layer Growth on Ge(100) via Spontaneous Chemical Reaction*, A. Kim,*** Korea Advanced Institute of Science and Technology (KAIST), Korea*; M.A. Filler,* Stanford University*; S.F. Bent,* Stanford University, US*; S. Kim,* KAIST, Korea, South Korea

We have demonstrated the layer-by-layer growth, via a urea coupling reaction between two bifunctional molecules, ethylene diamine and 1,4-phenylene diisocyanate, to form an ultrathin film on Ge(100)-2´1 at room temperature under vacuum conditions.@footnote 1@ The initial adsorption and subsequent growth of each layer was studied with multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy. Ethylene diamine reacts with Ge(100)-2x1 to produce a surface-bound amine group which is available for additional reaction. Subsequent exposure of 1,4 phenylene diisocyanate leads to a spontaneous urea coupling reaction between the surface-bound amine and highly reactive isocyanate functional group. Three bands at 1665, 1512, and 1306 cm-1 are characteristic of a urea linkage and provide evidence of the coupling reaction. The coupling procedure can be repeated in a binary fashion to create covalently bound ultrathin films at room temperature and, in the present work, we demonstrate the successful growth of four layers. In addition, we have found that an initial exposure of 1,4-phenylene diisocyanate to Ge(100)-2x1 produces an isocyanate-functionalized surface which, upon exposure to ethylene diamine, also forms urea linkages. This layer-by-layer deposition method provides a strategy with which to design and produce precisely tailored organic materials. @FootnoteText@ @footnote 1@ Kim, A.; Filler, M. A.; Kim, S.; Bent, S. F.; J. AM. CHEM. SOC. 2005, 127, 6123-6132

9:40am **SS2-ThM5 Alkylation of Silicon and Germanium Surfaces*, S. Rivillon*,** *Y.J. Chabal,* Rutgers University

Chemical modification of semiconductor surfaces is used to modify the surface properties and to provide new functionality. In particular, the formation of self-assembled monolayers (SAM) can lead to a broad range of applications such as micromechanical systems (MEMS), biosensors, lithography, and growth of alternative dielectrics without an interfacial oxide. To date, most work has been performed on silicon surfaces for which wet chemical cleaning methods have been well developed. In this talk, we focus on the alkylation of H- and Cl-terminated Ge surfaces, with close comparison to results of similar treatments on Si surfaces. Using infrared absorption (IR) spectroscopy, we have show that while HF-etched Si(100) and Ge(100) are atomically rough, the distribution of hydride species is different: hydrogen-terminated Si(100) exhibits mono-, di- and tri-hydride species, while H-Ge(100) only exhibit Ge-H and Ge-H@sub2@ species. The stability of both semiconductor surfaces to air is also different: for H-Si(100), oxygen is slowly incorporated into the substrate, forming O@sub3@-Si-H; for H-Ge(100), little oxidation takes place. Instead, hydrocarbons react with the hydrogen forming Ge@sub2@=CH@sub2@. This propensity of the Ge surfaces for alkylation has been used and comparison with silicon indicates that methoxylation takes place more rapidly on Ge surfaces.

10:00am **SS2-ThM6 Correlation of Surface Electronic Structure with Organic Reactivity on Si(114)*, D.E. Barlow*,** *A.R. Laracuente, L.J. Whitman, J.N. Russell,* Naval Research Laboratory

Si(114)-(2x1) is a stable high-index surface oriented 19.5° between (001) and (111). The equilibrium surface reconstruction is comprised of parallel rows of dimers, rebonded atoms, and tetramers, with all the rows oriented along the same crystallographic direction.@footnote 1@ The different Si(114) structural motifs within each row have distinct electronic

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[1] **Morton S. Traum Award Finalist**

[2] **Morton S. Traum Award Finalist**

structures, making this surface an ideal template for studying the relationship between adsorption site geometry (including symmetry), local electronic structure, and chemisorption of organic molecules on clean silicon surfaces. In this study, we have experimentally characterized the effects of charge transfer, @pi@ bonding, orbital symmetry, and di-radical reaction pathways on the cycloaddition chemisorption of ethylene on Si(114)-(2x1). Transmission FTIR spectroscopy was used to confirm the basic chemical structure and orientation of the chemisorbed ethylene. The results indicate a di-@sigma@ bonded product with a C-C bond axis preferentially oriented along the row direction. Using atomic-resolution STM, we identified three common adsorption structures located at the dimer, rebonded atom, and tetramer sites. In correlation with the FTIR results, these structures can be identified as [2+2] cycloaddition products, bridged rebonded atoms, and [4+2] cycloaddition products, respectively. The order of site reactivity is found to be rebonded atoms > dimers > tetramers. Reasons for this reactivity trend will be discussed. @FootnoteText@ @footnote 1@S. C. Erwin, A. A. Baski, and L. J. Whitman, Phys. Rev. Lett. 77, 687 (1996).

10:20am **SS2-ThM7 Contact Formation with a Single Molecule: 1,3-cyclohexadiene on the Si(100) Surface***, B. Naydenov, L.C. Teague, P. Ryan,* ***J.J. Boland,*** Trinity College Dublin, Ireland **INVITED**

We have studied the contact formed between a 1,3-cyclohexadiene (1,3-CHD) molecule on Si(100) and a Pt STM probe tip at 5 K. DFT studies indicate that the STM images obtained are the result of a specific probe-molecule interaction. This is confirmed by measurements of local barrier heights acquired at different probe-molecule separations and the associate change in the vibrational spectra measured at each separation. On this basis, we provide a detailed analysis of the physical and chemical interactions that accompany contact formation in this molecular system.

11:00am **SS2-ThM9 Surface Functionalization of Si(100)2x1 by Halogenated Ethylenes: Formation of C2-dimer, Vinylene, Vinylidene, and their Halogenated Derivatives***, K.T. Leung,* ***X.J. Zhou,*** University of Waterloo, Canada

Our recent studies on halogenated ethylenes on Si(111)7x7 and Si(100)2x1 have demonstrated the importance of a competing insertion mechanism to the commonly observed cycloaddition mechanism for Si surface functionalization. The combination of the C=C bond with Cl atoms provides interesting molecular platforms for investigating various novel effects involving different molecular symmetries and structures, Cl content and structural chemistries. The adsorption of these chlorinated ethylenes and their subsequent thermal chemistries on Si single-crystal surfaces can be used to generate ordered arrays of novel adspecies, including tetra-@sigma@ bonded C2 dimer (>C=C<), di-@sigma@ bonded vinylene (-HC=CH-) and vinylidene (>C=CH@sub 2@), and mono-@sigma@ bonded vinyl (-HC=CH@sub 2@) adspecies as well as their chlorinated homologs. We also show that purification of one of these C=C containing arrays could be achieved by simple manipulation of the annealing temperature or by post-exposure of H atoms. @FootnoteText@ * Work supported by the Natural Sciences and Engineering Research Council of Canada.

11:20am **SS2-ThM10 Infrared Spectroscopy Study of Adsorption of Maleic Anhydride on Si(100)***, Y. Kimura, H. Ishii,* ***M. Niwano,*** Tohoku University, Japan

The adsorption of maleic anhydride on Si(100)-2Ã-1 has been investigated using infrared absorption spectroscopy (IRAS) in the multiple internal reflection (MIR) geometry. Previously, it has been suggested on the basis of HREELS data that at low coverages the adsorption of maleic anhydride occurs through cycloaddition of the C=C bond to the dangling bonds of Si-Si dimers, and at high coverage, maleic anhydride dissociatively adsorbs on the Si(100) surface. In the latter case, the dissociated hydrogen is bound to the Si surface atoms to form the Si-H bond, and the remaining fragments are bound to the Si surface atoms via a single Si-C linkage with retention of C=C double bond. In this study, we observe that an intense absorption peak appears at 2125 cm-1, while the peak due to the C=O stretching vibration is relatively weak. Previously the 2125-cm-1 peak has been assigned as being due to the Si-H stretching vibration mode. However, this peak is positioned at a slightly higher frequency than the monohydride peak that shows up around 2080 cm-1. Furthermore, we observe that the 2125-cm-1 peak appears even when the Si(100) surface is dosed with deuterium-substituted maleic anhydride. From these observations, we suggest that upon adsorption the five-membered ring of maleic anhydride is broken to generate the C=C=O bond and the dissociated molecule is bound to the surface Si atoms via the C-O-Si linkage. Ab initio cluster calculations indeed predicts that the C=C=O bond exhibits a vibration mode around 2120 cm-1. The present results indicates that maleic anhydride dissociatively adsorbs on the Si(100) surface in a rather complicated manner.

11:40am **SS2-ThM11 Formation of Unsaturated Hydrocarbon Moieties on Hydrogen-terminated Si(111) by Grignard Reaction***,* ***T. Yamada,*** *K. Shirasaka, M. Noto, H.S. Kato,* RIKEN, Japan*; M. Kawai,* RIKEN and The University of Tokyo, Japan

Unsaturated hydrocarbon moieties, such as CH@SUB 2@=CHCH@SUB 2@-, CH:::C-,CH@SUB 3@CH=CHCH@SUB 2@- and CH@SUB 2@=CH- was deposited on hydrogen-terminated H:Si(111) by using the corresponding Grignard reagents (CxHyMgBr or CxHyMgCl) dissolved in tetrahydrofuran, followed by rinsing in CF@SUB 3@COOH solution. The product adsorbates were examined by vibrational methods with HREELS and internal multiple infrared reflection-absorption spectroscopy. It is anticipated that the unsaturated bonds within moieties may directly react with H:Si(111)@footnote 1@ and may be destroyed besides the desired bond shifting of C-Mg to C-Si. The CH@SUB 2@=CHCH@SUB 2@:Si(111) adsorbate was detected as the H-C= stretching and out-of-plane bending signals after the reaction in CH@SUB 2@=CHCH@SUB 2@MgBr/THF at 35°C for 5 min. The uptake of hydrocarbon moieties was 10% of surface Si with the remainder of originally terminating H atoms. The existence of C-Si stretching signal was revealed by using D:Si(111). Similarly in the cases of CH:::C- and CH@SUB 3@CH=CHCH@SUB 2@-, the unsaturated bonds were reserved. The double bond within CH@SUB 2@=CH- adsorbate was never observed, presumably because the C=C part would be close enough to the H-Si sites to undergo the direct adsorption. A notable result for better understanding of mechanism is that Grignard deposition just need one single H-Si site with no need for adsorption of MgX species in all cases. This was examined by isotope labeling in the rinsing procedure. Reservation of unsaturated bonds provides an approach to functionalized hydrocarbon moieties by addition reactions. Addition of NH@SUB 2@-, OH- or -COOH groups is prospective in surface modification with biochemical polymers with well-controlled adsorbate structure.@footnote 2@ @FootnoteText@ @footnote 1@M. R. Linford et al., J. Am. Chem. Soc. 117 (1995) 2145.@footnote 2@T. Yamada, et al., J. Chem. Phys. 121 (2004) 10660.

Surface Science

Room 203 - Session SS3-ThM

Reactivity of Bimetallic Surfaces

Moderator: R.A. Bartynski, Rutgers University

8:20am **SS3-ThM1 Temperature Effects on the Nucleation and Growth of Ag Films on 5-fold Surfaces of Icosahedral Al-Pd-Mn Quasicrystal***,* ***B. Unal,*** Iowa State University*; T.A. Lograsso, A.R. Ross,* The Ames Laboratory*; C.J. Jenks, J.W. Evans, P.A. Thiel,* Iowa State University and the Ames Laboratory

Growth of thin films on surfaces of complex intermetallics, such as quasicrystals, can provide new insights into nucleation, growth, and the thermodynamic factors that control film structures. We have used scanning tunneling microscope to study the growth and nucleation of the first few monolayers of Ag on the fivefold surface of an icosahedral Al-Pd-Mn quasicrystal surface at different temperatures. While Ag films grow layer by layer at 127K and 200K, the growth mode switches at about room temperature. Between 300 and 365 K, the Ag segregates in islands that are 4 and 5 monolayers high, on the terraces. When the temperature reaches 420K, islands grow at the step edges rather than on the terraces. This behavior will be discussed in terms of the existence of different types of diffusion barriers on the quasicrystal surface.

8:40am **SS3-ThM2 Pd-Au Model Catalysts: From Planar Surfaces to Nano-clusters***,* ***K. Luo,*** *C.-W. Yi, T. Wei, D.W. Goodman,* Texas A&M University

Pd-Au bimetallic model catalysts were synthesized as planar surfaces and as well-dispersed alloy clusters on Mo(110) and SiO2 ultra-thin films, respectively, under ultrahigh vacuum (UHV) conditions. The surface composition, geometric and electronic structures, and CO adsorption properties have been characterized using ion scattering spectroscopy (ISS), X-ray photoelectron spectroscopy (XPS), infrared reflection absorption spectroscopy (IRAS), and temperature programmed desorption (TPD). Stable Pd-Au alloy surfaces, where the surface is significantly enriched in Au relative to the bulk, are obtained upon sequential deposition of Pd and Au followed by an anneal. Characteristic isolated Pd sites are identified on the Pd-Au planar and supported Pd-Au clusters. Ethylene absorption and dehydrogenation show a clear structure-activity correlation with respect to these Pd-Au model surfaces.

9:00am **SS3-ThM3 Site-Directed Chemistry at Pt-Sn Alloy Surfaces***, **B.E. Koel**,* University of Southern California **INVITED**

Achieving higher activity and selectivity of heterogeneous catalysts, electrocatalysts, and sensors requires advances in controlling structure and chemistry relevant to interfacial reactions at the nanoscale. One can now exploit an unprecedented ability to investigate such phenomena on alloy surfaces to obtain new information about how and why composition, structure, and defects alter chemical reactions that occur at specific sites. We have been probing this site-directed chemistry at alloy surfaces in a wide range of chemisorption and catalytic reactivity studies. The talk today will focus on how recent results for several Sn/Pt(111) and Sn/Pt(100) ordered surface alloys have helped to define the overall chemical reactivity of Pt-Sn bimetallic surfaces, clarified the role of a second metal in altering the chemistry of Pt alloys, and led to general principles for understanding the reactivity and selectivity of alloy catalysts. Specifically, I will discuss exploiting Pt-Sn alloys for selective hydrogenation of 1,3-butadiene based on studies of well-defined model catalysts, i.e., Pt(111) and the (2x2)-Sn/Pt(111) and (@sr@3x@sr@3)R30°-Sn/Pt(111) surface alloys, that probe the influence of alloyed Sn on the reaction barrier to butadiene hydrogenation and the effect of surface Sn concentration on hydrogenation activity and selectivity. Fundamental concepts emerging from such studies enhance our understanding and ability to tailor local properties of alloy surfaces, which should facilitate the design of new catalysts and sensors.

9:40am **SS3-ThM5 Probing Complex Adsorption Structures: A Joint Experimental and Theortical Study of Prenal Adsorbed on Pt(111) and Pt-Sn Surface Alloys***, **J. Haubrich**[1],* University of Bonn, Germany*; D. Loffreda, F. Delbecq, P. Sautet,* Ecole Normale Supérieure de Lyon, France*; A. Krupski, C. Becker, K. Wandelt,* University of Bonn, Germany

Studies on catalysis such as the selective hydrogenation of @alpha@,@beta@–unsaturated aldehydes on transition metal surfaces represent a challenge to both experimentalists and theoreticians. Although numerous studies have been dedicated to systems like acrolein or prenal on Pt(111) in recent years, the details of the molecule-surface bonding still remain under debate. Yet the selectivities of such processes depend crucially on the adsorption complexes. Their characterization is even more complicated when alloy surfaces are considered because alloying is often used to optimize the properties of the catalyst. We here present a joint experimental and theoretical study on molecule-surface bonding of prenal on Pt(111) and two Pt-Sn surface alloys based on the interpretation of HREEL spectra using ab initio density-functional theory (DFT). Additionally TPD and LEED studies of prenal adsorbed at 100K on these surfaces were performed. While on Pt(111) the desorption of prenal is detected at 160K (multilayer) and 199K, also fragmentation reactions are observed giving rise to desorption of H@sub 2@ and CO. On Pt@sub 2@Sn and Pt@sub 3@Sn/Pt(111) this fragmentation process is suppressed. The HREELS experiments were carried out between 100K and 500K on Pt(111) show highly complex spectra of the adsorbed prenal and its fragments, which can be detected above 300K. On both Pt-Sn surface alloys very similar HREEL spectra of prenal are recorded. Combining the HREEL spectra with the results of the vibrational analysis obtained from the DFT calculations, we are able to identify stable adsorption geometries, interpret the normal modes corresponding to the measured loss peaks and to point to likely reaction intermediates.

10:00am **SS3-ThM6 Catalytic CO Oxidation at 70 K on a Au/Ni Surface Alloy***, **D.L. Lahr**,* MIT*; S.T. Ceyer,* MIT, US

A Au/Ni surface alloy catalyzes the oxidation of CO at low temperature by at least three distinct mechanisms. At the lowest temperature of 70 K, molecularly adsorbed O@sub 2@, spectroscopically characterized by high resolution electron energy loss spectroscopy as peroxo or superoxo species bound at multiple sites with vibrational frequencies of 865 and 950 cm@sup -1@, are the reactants with CO. A third molecularly adsorbed O@sub 2@ species, characterized by an O-O stretch mode at 790 cm@sup -1@, does not react with CO. Between 105-125 K, CO@sub 2@ production coincides with O@sub 2@ dissociation, suggesting a "hot atom" mechanism in which an O atom, formed upon dissociation of adsorbed O@sub 2@, reacts with CO before equilibrating with the surface. The CO that reacts is characterized by a C=O stretch mode at 2170 cm@sup -1@. Given the relatively high frequency, the reacting CO is likely bound to a Au atom. Above 125 K, CO bound to Au reacts with atomically adsorbed O atoms, characterized by a O-Au stretch mode at 660 cm@sup -1@. These results show that nanosize Au clusters bound to oxide supports are not a necessary condition for Au catalyzed, low temperature CO oxidation. In addition, the lower temperature at which the CO oxidation reaction occurs on the Au/Ni surface alloy as compared to the reaction temperature (~200 K) on the supported Au nanoclusters demonstrates that the activation energy is significantly lower on the Au/Ni surface alloy than on Au nanoclusters.

10:20am **SS3-ThM7 The Chemical Properties of Pd-Au Alloy Surfaces***, **T. Wei**, J.H. Wang, C.-W. Yi, D.W. Goodman,* Texas A&M University

The chemisorptive behavior of CO on Pd-Au alloy films and silica-supported Pd-Au nano-clusters has been studied by infrared reflection adsorption spectroscopy (IRAS). The relative influence of geometric versus electronic effects has been addressed by comparing the alloy and single component surfaces. A unique CO vibrational feature at 2088 cm-1 , corresponding to CO adsorbed on isolated Pd sites on Au, is clear evidence of an ensemble effect. On the other hand, the IRAS data for CO adsorbed on Pd-Au alloy surfaces show no evidence for an electronic effect of Au on Pd. The surface concentration of isolated Pd sites can be controlled by systematically altering the Pd-Au alloy composition, allowing detailed studies of isolated Pd sites as active sites for adsorption and reaction.

10:40am **SS3-ThM8 Unoccupied Electronic Structure and CO Adsorption in Ni/Cu(100) System***, **H. Yao**, S. Rangan, A.G. Danese, R.A. Bartynski,* Rutgers University

Ultrathin (i.e. several monolayers thick) metal films in the nanometer thickness range exhibit quantum size effects in their electronic structure. These effects often lead to interesting magnetic, optical or chemical properties. The particular materials selected in our work here Ni/Cu(100) system are motivated by two main reasons: First, because its applications in spin valve structures; second, we would expect that the study of this system will help us to understand the anomalous downward dispersion of unoccupied states in Cu/Ni/Cu(100) systems. We performed a series of inverse photoemission (IPE) studies of the unoccupied electronic structure of the Ni/Cu(100) and CO/Ni/Cu(100) systems as a function of Ni thickness. IPE spectra from Ni films exhibit very rich structures. A phase accumulation model (PAM) calculation suggests only one of the three main features is consistent with metallic quantum well (MQW) State in Ni film. CO adsorption strongly modifies the spectrum by dramatically suppressing one of the main features indicating that this feature is a Ni surface resonance. Furthermore, by comparing spectra from Ni/Cu(100) with results from Cu/Ni/Cu(100), we suggest the third feature is a state confined to the Ni/Cu interface, and the Cu/Ni interface state plays key roles in the anomalous dispersion of the unoccupied states in the Cu/Ni/Cu (100) system. The correlation between chemisorption properties of Ni films of different thickness and their electronic structures are studied with Temperature Programmed Desorption (TPD) and IPE. First principles calculations illustrating the evolution of the electronic structure of Ni/Cu structures as a function of both Ni and Cu film thickness will also be presented and compared to the experimental measurements.

11:00am **SS3-ThM9 Atomically and Time Resolved Pattern Formation in Strained Metal Films: S on Submonolayer Ag/Ru(0001)***, **B. Diaconescu**,* University of New Hampshire, US*; K. Pohl,* University of New Hampshire

Strained metallic interfaces can lead to highly ordered misfit dislocation networks that can be utilized as a bottom-up patterning method for the growth of cluster arrays of specific size and density. The great potential of this natural templating method is that the characteristic length scales are predicted to depend on the interfacial stress. 2D sulfur cluster growth on the misfit dislocation network of submonolayer Ag on Ru(0001) relaxes the 6nm x 4nm unit cell of the strained Ag film into a large-scale ordered triangular array of S filled vacancy islands, 5nm apart.@footnote 1@ Variable Temperature STM and LEED studies reveal that 2D S cluster growth takes place in two regimes: (1) At low S coverage a dilute phase of S clusters, etched at the threading dislocation sites of the Ag film forms. S clusters have an average size of 1.5nm@super 2@ corresponding to two S atoms per cluster, and a highly temperature dependent mobility. (2) At a S coverage above 0.018 ML the solid S cluster phase forms after all the available threading dislocation sites of the Ag film were etched. In this regime the highly ordered S cluster array shows a S coverage dependent cluster size and a p(2x2)S/Ru(0001) structure. In the growth process S partially relieves the strain in the Ag film as seen by the relaxation of the misfit dislocation network. For S coverage beyond 0.33 ML on the Ru(0001) terrace, the compressed S phase pushes Ag atoms into the second layer and the ordering of the S clusters is partially destroyed. It is found that exchange-induced inhomogeneous nucleation of S adatoms modifies the interfacial stress in the submonolayer Ag/Ru(0001) film and, that the size of

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[1] **Morton S. Traum Award Finalist**

the S-filled vacancy islands in the ordered self-assembled array can be controlled with S coverage. @FootnoteText@ @footnote 1@ K.Pohl et al. Nature 397, 238 (1999)@footnote *@ Supported by NSF-CAREER-DMR-0134933 and ACS-PRF-37999-G5.

11:20am **SS3-ThM10 Experimentally and Theoretically Determined Core-Level Shifts for Ultrathin Pd, Ag and AgPd Films on Ru(0001)***, **J. Onsgaard**, L. Bech,* Aalborg University, Denmark*; W. Olovsson,* Uppsala University, Sweden*; I. Abrikosov,* Link@um o@ping University, Sweden

Ultrathin composed metal films deposited on a relatively inert substrate are complex systems that are subject to both thin-film and surface-alloying effects. The evolution during build-up of ultrathin films of Pd and/or Ag deposited on Ru(0001) was followed by means of synchrotron-based photoelectron measurements (PES) of the valence band and of the Pd and Ag 3d5/2 core levels. Similarly, the evolution during stepwise annealing of ultrathin films of Ag and Pd deposited one-by-one on Ru(0001) was followed. LEED was applied to gain information on the atomic structure. The sample temperature was close to room temperature during data acquisition, whereas it typically was kept at ~550 K during metal exposures. Characteristic changes observed during film growth and annealing will be demonstrated. Further, experimentally obtained core level PES measurements will be compared with results of Density Functional Theory (DFT) calculations, which are based on the coherent potential approximation (CPA) and carried out within the complete screening picture, which includes both the initial and final state effects of PES.

11:40am **SS3-ThM11 The Photoemission Study of Oxygen Adsorbate on Pt@sub 3@Ni (100), (110), and (111) Surfaces***, **B.S. Mun,*** Lawrence Berkeley National Laboratory, US*; M. Watanabe, M. Rossi, V. Stamenkovic, N.M. Markovic, P.N. Ross,* Lawrence Berkeley National Laboratory

The electronic structures of oxygen covered surfaces on Pt@sub 3@Ni (100), (110), and (111) alloys are studied with photoemission spectroscopy. The positions of local d-band center and the widths from valence band density of state (DOS) measurements are compared before and after the oxygen adsorption at various temperatures. The correlations between the electronic structures of oxygen-adsorbed surfaces and the chemical properties are discussed. Modified electronic structures of Pt@sub 3@Ni surfaces are also compared to those of Pt single crystals surfaces. The density functional theory calculation is carried out for the comparison of the experimental results to the theory.

Thin Films

Room 306 - Session TF-ThM

Optical Thin Films

Moderator: C. Stoessel, Consultant

8:20am **TF-ThM1 Refractive Index Control of Sputtered Multicomponent Bismuthate Glass Films for Bi-EDWA***, **J. Kageyama**, Y. Kondo, M. Ono, N. Sugimoto,* Asahi Glass Co., Ltd., Japan

Multicomponent bismuthate glass films were deposited from a glass target by radio frequency planar magnetron sputtering for fabricating bismuthate erbium doped waveguide amplifier (Bi-EDWA).@footnote 1, 2@ It is essential to control the refractive index of the film, because it affects the beam propagation in optical waveguide structure. The appropriate refractive index difference between the core and the cladding of Bi-EDWA is about 0.03. Thus it is desired that the batch-to-batch reproducibility of refractive index is less than 0.001. The refractive index of the film is mostly stable during the beginning of target life, however it decreases as the total sputtering time increases. In this work, it was revealed that the main reason why the refractive index varies is not the change of cationic composition in the film, but the increase of oxygen concentration in the film as the deposition rate decreases. It was also found that the decrease of deposition rate is caused by the decrease of sputtering rate. Additionally it was considered that the decrease of sputtering rate is linked with the decrease of self bias voltage at the target as the target becomes thinner. We also examined the effect of new magnetic circuit having an improved magnetic alignment and a lower magnetic flux density to make the above-mentioned film properties stable. As a result, we succeeded in obtaining good reproducibilities of refractive index and deposition rate dramatically. It is expected that this method is widely applied in sputtering of insulating films and effective for suppressing the decrease of deposition rates and the variation of film properties. @FootnoteText@ @footnote 1@ Y. Kondo, M. Ono, J. Kageyama, M. Reyes, H. Hayashi, N. Sugimoto, Proc. OFC/NFOEC 2005, Anaheim, CA, USA, PDP2. @footnote 2@ Y. Kondo, M. Ono, J. Kageyama, H. Hayashi, M. Reyes, N. Sugimoto, Electron. Lett. 41, 317 (2005).

8:40am **TF-ThM2 Controlled Doping and Photoluminescence Properties of Er-doped Yttrium Oxide Thin Films***, **T.T. Van**[1],* University of California, Los Angeles*; J. Bargar,* Stanford Synchrotron Radiation Laboratory*; R. Ostroumov, K. Wang, J.P. Chang,* University of California, Los Angeles

Though silica has traditionally been used as the Er host in fiber amplifiers, it is an unsuitable host in small, compact amplifiers due to its low solubility for Er. One potential host is Y@sub 2@O@sub 3@. Its high refractive index allows for a compact geometry and large signal admittance angle, thus higher pumping efficiency. Due to the similarities in crystal structure and lattice constant between Y@sub 2@O@sub 3@ and Er@sub 2@O@sub 3@, a much higher Er concentration can be incorporated Y@sub 2@O@sub 3@, compared to that in silica. Er-doped Y@sub 2@O@sub 3@ thin films were synthesized by radical-enhanced atomic layer deposition (RE-ALD) at 350°C, using metal beta-diketonates as the metal precursors and O radicals as the oxidant. The deposition of Y@sub 2@O@sub 3@ was alternated with Er@sub 2@O@sub 3@ and the Er doping level was effectively controlled by varying the ratio of Y@sub 2@O@sub 3@:Er@sub 2@O@sub 3@ cycles. The films were polycrystalline with a preferential growth in the (111) plane. Room-temperature PL at 1.54 µm was observed in a 500-Å Er-doped (6.6 at.%) Y@sub 2@O@sub 3@ film, showing well-resolved Stark features indicating the proper incorporation of Er in Y@sub 2@O@sub 3@. The result is very promising, since the film is fairly thin and no annealing at high temperature is needed to activate the Er ions. Extended X-ray absorption fine structure (EXAFS) analysis showed an identical Er local environment for samples with 6-14 at.% Er, suggesting the PL quenching at high Er concentration (>12 at.%) is likely dominated by ion-ion interaction and not by clustering. The effective absorption cross section for Er in Y@sub 2@O@sub 3@ was estimated to be on the order of 10@super -18@ cm@super 2@, about three orders of magnitude larger than that in the silica host. These results validate Y@sub 2@O@sub 3@ as a promising Er host and demonstrate that RE-ALD is a viable technique for synthesizing thin films with well-controlled dopant incorporation.

9:00am **TF-ThM3 Alternating Current Thin Film Electroluminescence (ACTFEL) from Zinc Sulfide Doped with Rare Earth Fluorides***, **D.M. DeVito**, A.A. Argun, M.R. Davidson, P.H. Holloway,* University of Florida

Thin film electroluminescent (EL) devices are an excellent source for efficient infrared emission. A wide variety of applications exist for infrared emitters, including therapeutic medical treatment, chemical analysis, infrared displays and telecommunications. Rare earth elements, such as erbium, thulium and holmium are ideal choices for dopants in phosphors because they possess a number of sharp transition in the infrared region from 850-2800nm. These rare earth dopants also emit in the visible region (400-700 nm) and have been used in a variety of visible display technologies. Zinc sulfide is a suitable semiconductor host material because it is chemically stable, possesses a bandgap of 3.6 eV at 300 K and is therefore transparent to visible and NIR photons, and provides a lattice in which electrons can be excited to ballistic energies in order to excite emission from rare earth dopants. Thin films, approximately 0.8 microns thick, of rare earth doped ZnS were RF magnetron sputter deposited at 120 W from dual targets of undoped ZnS and rare earth fluoride doped ZnS. Deposition temperature, duty cycle, sputter gas pressure and post-deposition annealing temperature were varied in a design-of-experiment to optimize the ratio of near-infrared to visible emission. Suppression of visible emission can result in energy transfer into the infrared transitions and higher NIR/visible intensity ratios. Post-deposition annealing is a key parameter for increasing this ratio, and temperatures between 350°C and 525°C for 1 hour in N@sub 2@ show good results. Maximum EL radiance for ZnS:ErF@sub 3@ at 1550 nm was increased from ~1 µW/cm@super 2@ before annealing to 28 µW/cm@super 2@ post-anneal. The optimum concentrations of both rare-earth ion and fluorine were determined by EDS and SIMS analysis.

9:20am **TF-ThM4 Custom-design of Optical Thin Films of Silicon Oxide by Direct Write Deposition***, **H.D. Wanzenboeck**, M. Fischer, E. Bertagnolli,* Vienna University of Technology, Austria

The fabrication of optical transparent thin films on specific areas has gained increased interest due to optical interconnect concepts. Robust, inorganic materials such as silicon oxide provide optical interconnects with a high bandwith and a fast, power-saving data transmission. Moreover, the fabrication of transparent thin films is also desirable for the modification of

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[1] **TFD Student Award Winner**

optical photomasks. This work describes a rapid fabrication approach of thin silicon oxide films on confined areas by direct-write deposition. This maskless process utilizes the localized chemical vapor deposition on specific areas utilizing a focused electron beam. The deposition from siloxane vapor in presence of oxygen is initiated by the energy of the electron beam with a 5 nm diameter. By scanning the beam, thin films with arbitrary geometry and 3-dimensional structures were deposited. The process was optimized towards a high deposition rate and high material purity. The influence of process parameters on the deposition efficiency is discussed. A characterization of the chemical composition and of the surface roughness was performed with AES and AFM respectively. The optical properties were investigated by infrared and UV/Vis spectroscopy. The correlation to processing conditions and the growth mechanism is discussed. The electrical features of silicon oxide were tested with a metal-insulator-metal capacitor setup. This work illustrates the flexibility of this maskless method and the potential to control material properties via the process parameters. The fabrication of exemplary structures such as 3-dimensional silicon oxide rods, transparent films in trenches and networks of silicon oxide wires illustrate the application potential of this versatile direct-write method.

9:40am **TF-ThM5 Vacuum-Deposited Form-Birefringent Materials for Use as Retarders and Polarizers***, **I.J. Hodgkinson**,* University of Otago, New Zealand **INVITED**

Vacuum-deposited form-birefringent films are of special interest today due to their potential use as trim retarders for front and rear projection TV systems. The presentation reviews basic computational methods, deposition geometries, and experimental techniques for characterizing nanostructures, optical performance and physical properties. As well several related developments are discussed, including multilayered birefringent coatings, birefringent arrays and chiral coatings deposited as twisted stacks of birefringent layers.

10:20am **TF-ThM7 Birefringent Films for Contrast Enhancement of LCoS Projection Systems***, **K.D. Hendrix**, M. Duelli, D.M. Shemo, K.L. Tan,* JDS Uniphase **INVITED**

High performance projection displays based on LCoS panel technology have the potential to deliver very high contrast and performance at an attractive price. These systems use polarization-based light engines that utilize wire grid polarizers (WGP) and vertical-aligned nematic (VAN) LCoS panels. To achieve high contrast, the linear polarization state created by the WGP must be maintained in the dark state to prevent light leakage to the screen. However, the LCoS panel has a residual retardance, and without compensation, this leakage degrades the system contrast. We describe the design and contrast measurement results of a birefringent contrast enhancing component that compensates this residual retardance and improves the overall system contrast to 4500:1. The component is comprised of birefringent films with individually controllable a-plate and c-plate compensation, accurate retardance targeting and excellent uniformity for both retardance magnitude and orientation. The component also has good environmental durability and low defects.

11:00am **TF-ThM9 New Imaging Ellipsometric Techniques for Thin Film Dielectric Tensor Measurement***, **R.A. Chipman**,* University of Arizona **INVITED**

NO ABSTRACT SUBMITTED.

11:40am **TF-ThM11 Thin Film Optical Constants in the EUV using Simultaneous Reflection and Transmission Measurements***, D.D. Allred, **G.A. Acosta**, R.S. Turley, J.E. Johnson,* Brigham Young University*; K.R. Adamson,* Harvard University*; N. Farnsworth,* Brigham Young University

We discuss the use of variable-angle transmission/reflection measurements for determination of optical constants of thin films from 50 to 600 eV. Such techniques have been widely used in the visible portion of the electromagnetic spectrum, but are relatively less well known in the EUV and beyond. For this range, depositing a thin film on a transparent substrate is impossible since partially transparent films must be less than ~50 nm and transparent substrates are unknown. Instead we deposited films directly on the surface of a diode detector. We expanded the technique by measuring simultaneously, both reflection from, and transmission at, the same position on the diode to minimize errors stemming from film nonuniformity. Two materials so studied at CXRO's beamline 6.3.2 at the Advanced Light Source at the Berkeley National Laboratory were reactively sputtered thorium oxide and scandium oxide. We will report the complex index of refraction obtained by fitting this data for a number of energies in this range.

Applied Surface Science
Room 206 - Session AS+TF-ThA

Thin Film Characterization II

Moderator: K. Lloyd, Dupont

2:00pm **AS+TF-ThA1 C@sub n@ (50@<=@n<60) Films on HOPG***, **A. Böttcher**, P. Weis, S.-S. Jester, D. Löffler, M.M. Kappes,* Universität Karlsruhe, Germany

Novel solid materials have been grown under ultra high vacuum conditions by gentle deposition of C@sub n@@super +@ (50@<=@n<60) on HOPG surfaces (kinetic energy typically < 0.1 eV/atom). C@sub n@@super +@ ions resulting from the electron-impact induced ionization/dissociation of C@sub 60@ are driven by a system of electrostatic lenses through a mass spectrometer towards the HOPG substrate where an appropriate retarding potential assures their soft-landing. This setup enables to achieve deposition rates in the range of 10@super 12@ ion/s. AFM images reveal that the C@sub n@ films grow according to the Volmer-Weber scenario, i.e. the surface is initially dominated by 2D fractal islands, which in later deposition stages become 3D dendritic pyramids. This behavior stems from the aggregation of C@sub n@ cages, which is driven by reactive sites as formed by adjacent pentagons (or heptagons) on individual cages. The resulting covalent bonds are responsible for the unusually high thermal stability of the C@sub n@ films. Thermal desorption spectra of C@sub 58@ reveal activation energies around 2.2 eV, which are considerably higher than the sublimation enthalpy of C@sub 60@ films. AFM images taken after completing the desorption exhibit a network of highly polymerized cages, which remains stable even at temperatures around 1300 K. Recent DFT calculations as well as UPS-measurements support the aggregation scenario of C@sub n@ cages. Well recognizable features in the valence-band spectra allow identification of the band gap as well as contributions from C@sub n@-C@sub n@ bonds.

2:20pm **AS+TF-ThA2 An in situ Study on Amorphous Carbon Films and the Vapor Phase Lubrication in Magnetic Data Storage Media***, **Y. Yun**, A.J. Gellman,* Carnegie Mellon University

Amorphous carbon films have been used as a protection for the magnetic layer in hard disks for years. Perfluoropolyalkylether (PFPE) has been applied on the amorphous carbon film surface as lubricant during the crashing of the read-write head on the amorphous carbon film. The fundamental understanding of the thermal stability and oxidation kinetics of amorphous carbon films and the adsorption of PFPE lubricants is essential to obtain the ultimate high performance protection and lubrication. Vapor phase lubrication integrates the amorphous carbon film deposition and lubrication in vacuum. The amorphous carbon film can be oxidized under controlled conditions immediately prior to lubricant adsorption. The kinetics of oxidation has been studied using x-ray photoelectron spectroscopy in an UHV apparatus that allows oxidation of freshly deposited amorphous carbon films. The dissociative sticking coefficient of oxygen is ~10-6 and the oxidation kinetics can be described by a Langmuir-Hinshelwood mechanism. The vapor phase lubrication of amorphous carbon film has been emulated by absorbing (CF3CF2)2O and CF3CH2OH that serve as models for the fluorinated ether backbone and hydroxyl endgroup of PFPE lubricants. No decomposition was observed. The desorption energy of the hydroxyl endgroup is sensitive to the oxidation of the amorphous carbon film by air or O2. The increase of the desorption energy is proportional to the oxygen content on the amorphous carbon film surface. This indicates that the interaction between PFPE lubricant and the amorphous carbon film can be tailored by controlled oxidation of the amorphous carbon film. Vapor phase lubrication not only helps to probe the bonding mechanism of PFPE lubricant with amorphous carbon film, but also proposes a lubrication method which allows people to design and tune the bonding of PFPE lubricants with amorphous carbon films by controlled oxidization.

2:40pm **AS+TF-ThA3 Laser Processing of Polymer Nanocomposite Thin Films***, **A.T. Sellinger**, E.M. Leveugle, G. Peman, L.V. Zhigilei, J.M. Fitz-Gerald,* University of Virginia

Current biotechnology and sensor research has enhanced the drive to establish viable methods for depositing high quality organic and polymer thin films. In this research, solid targets of polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly-lactic co-glycolic acid (PLGA) were prepared for room temperature pulsed laser deposition (PLD). Likewise, frozen targets consisting of varying concentrations of PS, PMMA, and PLGA dissolved in a volatile matrix material were prepared for matrix assisted pulsed laser evaporation (MAPLE). Carbon nanotubes (CNTs) were subsequently added to both PLD and MAPLE target systems in upwards of 20 wt.% loading for deposition of polymer nanocomposite films. Targets were ablated using a 248 nm KrF laser at fluences ranging from 0.025 J/cm@super 2@ to 1.0 J/cm@super2@. In addition, polymer concentration in MAPLE targets was varied between 1 wt.% and 10 wt.% relative to the matrix solvent. Films were deposited on Si, SiO@sub 2@, and NaCl substrates at room temperature in an Ar atmosphere. The chemical properties of the films deposited by both methods varied significantly from the native, with changes in molecular weight on the order of 75%. While PLD produced films generally showed little observable morphology, MAPLE deposited films typically showed evidence of blistering. A molecular dynamics (MD) program developed to simulate ablation of a frozen target during MAPLE was utilized to model and predict experimental phenomena. Particularly, the ejection of clusters of PMMA and volatile matrix molecules was studied and related to the observed morphology of the deposited films.

3:00pm **AS+TF-ThA4 Thin Films of Fe on Pt(111) : Alloy Formation***, **M. Yoshimura**, S. Komaru, K. Ueda,* Toyota Technological Institute, Japan

Addition of transitional metals to Pt catalysts has been known to improve catalytic efficiency. Pt-Fe bimetallic catalysts attract attention in industrially important fields such as polymer electrolyte fuel cell (PEFC).@footnote 1@ Modification of geometrical and electronic structure of Pt surface would be responsible for the improved efficiency. Recently, Jerdev et al. examined Fe-Pt alloying processes by XPS and LEED.@footnote 2@ They found that heating thick Fe films on Pt result in an ordered alloy layer of 2 x 2 structure. However, detailed atomistic study has not been carried out. Here, we report scanning tunneling microscopy (STM) study on the growth of Fe on Pt(111) and the alloying processes by heating. All experiments were performed in ultrahigh vacuum of a base pressure below 2 x 10@super -8@ Pa. Pt surface was cleaned by cycles of Ar@super +@ ion bombardment at 1 keV and subsequent annealing in vacuum to 1300 K. Surface cleanliness was monitored by XPS and STM observation. Fe (99.999 %) was deposited onto the Pt(111) surface by an e-beam evaporator. STM observation was carried out at room temperature, and electrochemically etched tungsten tips were used. After 1.1 ML Fe deposition at room temperature, two-dimensional Fe islands up to three stories were formed and the Pt substrate was still visible, which is reasonable in terms of surface free energy. After annealing to 800 K, diffusion of Fe occurs and a network structure consisting of Fe and Pt atoms appears on the surface. After annealing to 1070 K, 2 x 2 structure was locally formed at the step edges, which corresponds to the reported alloy structure by Jerdev et al. It is also found that the surface includes defective structure as well as phase boundaries. The growth of Fe on Pt(111) as well as detailed alloying processes are discussed. @FootnoteText@ @footnote 1@ L-J. Wan et al., Chem. Comm. 2002 (2002) 58.@footnote 2@ D. I. Jerdev et al., Surf. Sci. 513 (2002) L391.

3:40pm **AS+TF-ThA6 Scanning Auger Microscopy of Alkylated Crystalline Silicon(111) Surfaces***, **H.M. Meyer III**,* Oak Ridge National Laboratory*; L.J. Webb,* California Institute of Technology*; D.F. Paul,* Physical Electronics*; N.S. Lewis,* California Institute of Technology

Silicon materials used in solar energy conversion devices must be prepared to a high degree of purity in order to prevent recombination of the photoexcited electron-hole pair. Recently, a wet chemical alkylation technique has been shown to result in an atomically-flat surface covered with bound alkyl groups preventing complete formation of silicon oxides at the surface even after exposure to oxidizing environments over long time periods. Surface charge carrier recombination velocities remain remarkably low, indicating that silicon oxides forming do not result in charge carrier trap states as previously observed on un-passivated, hydrogen-terminated Si(111). These results indicate that any detectible oxide is not growing in a uniform manner, but rather in small patches leaving large portions of the alkylated surface free of any oxide. Extensive x-ray photoelectron spectroscopic evidence on the chemical structure and reactions of these passivated surfaces has been collected over large areas of the surface. Scanning Auger microanalysis was used to map the oxidation of alkylated Si surfaces to determine if it was proceeding uniformly or in discrete areas. Preliminary results using a PHI 680 Scanning Auger Nanoprobe showed distinct patches of oxide less than 100 nm in width. The orientation of the oxide patches suggested that growth was occurring along step edges between flat terraces, leaving the terraces themselves chemically unaltered. Comparison of these early results were made with data obtained using PHI 700 Field Emission Scanning Auger Nanoprobe, a higher performance Auger Electron Spectroscopy (AES) system. The PHI 700 Schottky field emission optics offer Auger spatial resolution of less than

8nm and made it possible to image the oxide features more clearly. Further, the PHI 700 was able to image areas with comparable resolution as the PHI 680, but with less current and therefore less alteration of the oxide due to electron beam reduction.

4:00pm **AS+TF-ThA7 Electron Beam Induced Processes for Repairing Defects on Quartz Masks***, **M. Fischer**, J. Gottsbachner, S. Mueller, E. Bertagnolli, H.D. Wanzenboeck,* Vienna University of Technology, Austria

For conventional optical masks focused ion beam (FIB) has become a popular tool for repairing defects. A fundamental problem of using FIB for mask repair is the implantation of Ga-ions and the damage of the substrate surface. Especially for 248 nm and 193 nm lithography electron beam repair avoids the transmission loss which is generated by the implanted Ga-ions. This paper presents some promising results that demonstrate the feasibility of using electron beam induced processes for repairing defects on quartz masks. A commercial scanning electron microscope with a tuneable acceleration voltage of 0,1- 30 kV equipped with a gas inlet system was used to investigate a siloxane based deposition process of silicon oxides on quartz glass substrates. Siloxane together with an oxidizing reagent is decomposed by the electron beam on the surface of the quartz glass substrate. The process was optimized towards high material purity. A chemical investigation of the deposited structures was performed by Auger electron spectroscopy and EDX. The optical properties of the deposited material were investigated by infrared, UV/Vis and AIMS measurements. The influences of process parameters such as precursor gas combinations, precursor gas composition ratios, and electron beam parameters on the optical transparency were discussed. The electrical features of the deposited silicon oxide as dielectric material were tested with a metal-insulator-metal setup. A correlation between the electrical properties, the material purity and the optical transparency of the deposited silicon oxide structures is discussed. This work is considered a solid bias for a better understanding of electron induced deposition of silicon oxide and path the way of a further process optimization of this quartz glass mask repair technique.

4:20pm **AS+TF-ThA8 Extending Defect Root-Cause Analysis to sub-100nm in-film Particle Contamination***, **C. Lazik**, Y. Uritsky,* Applied Materials, Inc.

Scanning Electron Microscopy (SEM) in combination with Energy Dispersive X-Ray Spectroscopy (EDX) is essential for effective root-cause particle analysis in the semiconductor industry and forms the core of commercial defect review tools (DRT). In many cases, however, particularly for small (<0.1µm) in-film particles located within or under deposited films, the standard DRT approach is less straightforward because of (i) uncertainty in the position of the defect 'core' within the film and/or (ii) poor SEM contrast in dielectric films. These effects ultimately limit the assurance that the electron beam is focused on the defect "core" during automated spectrum acquisition. In addition, the defect geometry may preclude the subtraction of an EDX background spectrum. We present here several examples related to the analysis of ~ 50nm "bump" defects, each of similar surface morphology, encountered following the deposition of one or more dielectric films. Providing a suitable analysis of the particle cross-section enabled the classification of the defect based upon its location within the film-stack as well as the defect formation mechanism (e.g. gas-phase nucleation, arcing). In each case, the defects were analyzed initially by top-down SEM/EDX followed by cross-sectional analysis using the focused ion beam (FIB) with only limited success. Extended Auger (PHI Smart-300 DRT) and/or TEM analysis on FIB prepared samples proved critical in yielding accurate root-cause analysis. Details will be discussed in presentation, but the general conclusion is that the integration of FIB/TEM into the modern DRT platform is necessary.

Biomaterial Interfaces
Room 311 - Session BI-ThA
Bionanotechnology

Moderator: T.P. Beebe, University of Delaware

2:00pm **BI-ThA1 Strategies to Increase the Sensitivity of Biosensors based on the Light Absorption of Immobilized Metal Nanostructures***, **F. Frederix**, K. Bonroy,* IMEC, Belgium*; D. Saerens,* VUB, Belgium*; G. Maes,* KULeuven, Belgium*; S. Muyldermans,* VUB, Belgium*; G. Borghs,* IMEC, Belgium

The Transmission Plasmon Biosensor is a novel, cheap and easy-to-handle biosensing technique. It consists of immobilized metal nanoparticles that exhibit plasmon absorption peaks. This absorption is highly dependent on the size, the shape and the dielectric properties of the close environment of these nanoparticles and can therefore be used to perform biosensing. The nanoparticle films were realized using self-assembly techniques, thermal evaporation, electroless plating or soft-lithographic techniques. Mixed SAMs were used to couple antibodies to the nanoparticle films. The change in absorption properties of the nanoparticle films upon antibody-antigen binding was monitored in order to obtain quantitative information on the antibody-antigen interaction (prostate specific antigen). Besides the localised plasmon resonance sensing, we observed a novel physical phenomenon namely the intraband transition absorption enhanced sensing. Furthermore, the applied technique was identified to be a useful alternative for the most widely used clinical immunosensing technique, i.e. the ELISA technique. This promising alternative was applied onto modified microtitre plates, which allow for the implementation into an array technology. The Transmission Plasmon Biosensor fulfils therefore the needs of an ideal, multi-analyte bio(nano)sensor. However, the sensitivity could be a drawback of this sensing technique. We will show several strategies to increase the sensitivity to a diagnostically interesting concentration range (ng/mL range). These strategies will involve the use of camel antibodies to sense closer to the sensor surface (the sensitivity decreases exponentially away from the surface), the use of multiple nanoparticle films and nanoparticles with special morphologies. In addition, we will show that this sensing technique can be also applied for performing enzyme sensing and that it showed remarkable results for small molecule detection (antibiotics).

2:20pm **BI-ThA2 Impact of Composite Shell Thickness on Stability of Single Enzyme Nanoparticles***, **A.S. Lea**, J.B. Kim, J.W. Grate,* Pacific Northwest National Laboratory

Single-enzyme nanoparticles (SENs), comprised of individual alpha-chymotrypsin molecules surrounded by a porous organic/inorganic composite network less than a few nanometers thick, have been developed. The synthetic procedure, entailing enzyme modification and two orthogonal polymerization steps, yields nanoparticles containing a single enzyme. In stability experiments, the incorporation of these enzymes into the nanostructure dramatically increased its enzymatic stability. Furthermore, the nanoscale structure around the enzyme is sufficiently thin and porous that it does not impose a significant mass transfer limitation on the substrate. We have used tapping mode AFM (TM-AFM) to characterize single enzyme nanoparticles containing alpha-chymotrypsin (SEN-CT). Compared to transmission electron microscopy (TEM), TM-AFM resulted in much quicker and more accurate characterization of SENs since they are still in a hydrated state. We can tailor the thickness of the composite shell during the orthogonal polymerization steps in the synthesis of the SENs. The measured size-distribution of the different preparations was used to relate enzyme stability to the thickness of the porous composite shell. We will discuss this relationship in detail.

2:40pm **BI-ThA3 Vertically Aligned Carbon Nanofiber Array Integrated with Active-Addressed Thin Film Transistors for Intra/Extracellular Stimulus and Measurement***, **S.-I. Jun**, P.D. Rack,* The University of Tennessee*; T. McKnight, A.V. Melechko, M.L. Simpson,* Oak Ridge National Laboratory

Vertically aligned carbon nanofibers (VACNF) have been used as nanoscaled electrodes for electroanalysis and as nanostructured scaffolds for delivering biological material into live cells. Thin film transistors (TFTs) have long demonstrated their effectiveness for driving, switching, and read-out capabilities in many microelectronic applications. In this study, we have fabricated and characterized a 20X20 active matrix thin film transistor array with integrated vertically aligned carbon nanofibers grown from Ni catalyst by direct current plasma enhanced chemical vapor deposition (DC-PECVD). This integrated device provides great potential to perform direct cell sensing, probing, and recording with a high electrode density and active addressing. Consequently, actively addressed nanofiber arrays can offer bi-directional interfacing with tissue matrices using intercellular positioning of electrode elements as well as the potential for intracellular residence of probes within individual cells. For this device, each film in the TFT array was fabricated by an rf magnetron sputtering process with DC substrate bias at a substrate temperature below 200°C. In this presentation, we will demonstrate the process flow of the inverted metal-oxide-semiconductor field effect transistor and the nanofiber integration scheme. The electrical characteristics of the transistor will be discussed and the electrochemical characteristics of the TFT addressed array in various biological electrolyte solutions will be presented.

3:00pm **BI-ThA4 Dynamic Surface Modification and Patterning using Electrochemistry and Molecular Assembly Approach***, **C.S. Tang,*** Swiss Federal Laboratories for Materials Testing and Research (EMPA), Switzerland*; S. Makohliso, M. Heuschkel,* Ayanda Biosystems SA*; J. Voeroes, S. Sharma,* Swiss Federal Institute of Technology (ETH)*; B. Keller,* Swiss Federal Laboratories for Materials Testing and Research (EMPA), Switzerland*; M. Textor,* Swiss Federal Institute of Technology (ETH)

Microarray technology is a powerful and versatile tool commonly used in biochemistry and molecular biology. This miniaturized and parallelized technique has contributed significantly to bioanalytical processes such as large-scale genomic sequencing. One option for additional flexibility within a microarray is the use of electrochemical tools to dynamically influence and steer formation and properties of adsorbed molecular layers at the solid-liquid interface. By controlling and manipulating the placement of polyelectrolytes and biomolecules under the influence of an electric field, we have demonstrated that an electroactive biosensing platform with specificity and high sensitivity enable rapid screening and discrimination of different biomolecules with high selectivity. Using patterned substrates consisting of conductive areas in a non-conductive background, the electrically switchable surface can be modified to reversibly adsorb and release an adlayer of protein-resistant polymer. Macromolecules or biomolecules could be subsequently adsorbed onto the polarized indium tin oxide (ITO) microelectrodes by using simple surface chemistry. As a proof of concept, labeled functionalized polymer, proteins and vesicles were immobilized onto the ITO microelectrodes to produce a highly selective and heterogeneous microarray with specific electronic addressability. Some future applications with a localized addressable electronic microarray could include microfluidics, biosensors, drug delivery and manipulation of cellular neuron network for tissue engineering.

3:20pm **BI-ThA5 Fabrication of Bioconjugated Polymeric Nanostructures and Metal Nanowires by AFM Anodization Lithography***, W.-K. Lee, H. Ma, S. Chen, A. Chilkoti, **S. Zauscher,*** Duke University

Patterning of polymeric and biomolecular nanostructures on surfaces and the control of their architecture are critically important for the fabrication of biomolecular devices and sensors. Here we show for the first time how we use AFM anodization lithography to chemically modify polymer brushes directly to allow conjugation of biomolecules. Surface-confined non-fouling and protein resistant poly(oligo(ethylene glycol) methyl methacrylate) (pOEGMA) brushes were prepared on silicon substrates by surface-initiated atom transfer radical polymerization (ATRP) in a grafting-from approach. These pOEGMA brushes were then patterned directly on the nanoscale by AFM anodization lithography, generating nano-trenches with carboxylic acid functionality. Proteins were then immobilized on these nanopatterned areas by suitable coupling chemistries. We also show an intriguing approach to deposit gold onto silicon oxide patterns by field-emission from gold-coated AFM probes. We capitalize on this novel lithography approach to fabricate gold nanowires of arbitrary shape. Our unique nanofabrication approaches lead to novel types of nanostructures that can potentially be used as biosensors or as substrates for the precise presentation of biomolecular queues to cells. Furthermore, our gold nanostructures can be used for electrical connections, or as plasmonic structures for biomolecular sensing.

3:40pm **BI-ThA6 In-situ Microcontact Printing of Proteins***, **D. Mayer**, D. Schwaab, O. Salomon, A. Offenhaeusser,* Research Center Juelich, Germany*; A. Yasuda, J. Wessels,* Sony International (Europe) GmbH, Germany

Soft lithography appears to be a promising candidate among other techniques like electron beam-, ion beam- or x-ray lithography, in order to define structures below 100 nm. In contrast to the others, soft lithography has the advantage of being a relatively simple low costs technique. In addition, the technique can in principle be applied for large areas and therefore provides a fast lithography process. Furthermore soft lithography is fully chemical and bio-compatible. The main objective of the presented work is to establish a powerful technique in order to transfer biomolecules to functional surfaces with structure size beyond the limit of photolithography. On this account we have developed a novel in-situ approach for the patterned transfer of proteins. The proposed technique is a modification of the commonly used Microcontact Printing (@mu@CP). The main derivative is that all transfer steps are performed under physiological conditions. For testing the capabilities of in-situ Microcontact Printing we have used horse heart cytochrome c (cyt c) as model molecule. Electrochemical investigations were performed to compare the conventional and the new in-situ @mu@CP method by measuring the redox activity of cyt c transferred with different techniques. We succeeded to print proteins under conservation of their structural integrity and functionality, while the activity of molecules transferred with conventional @mu@CP is much lower. In addition we will demonstrate by means of surface scanning microscopy methods that this technique is also capable of transfer patterns with a critical dimension of 150nm.

4:00pm **BI-ThA7 Microfluidic Neuronal Culture Device for Neuroscience Research***, **N.L. Jeon,*** University of California, Irvine **INVITED**

This presentation will describe a novel microfabricated neuronal culture device and its application in Alzheimerâ?Ts Disease and Axonal Regeneration research. The device combines microfabrication and surface micropatterning approaches to create a multi-compartment neuronal culturing platform that can be used in a number of neuroscience applications. A replica-molded PDMS is placed on a tissue culture dish (polystyrene) forming two or more fluidically isolated compartments. These compartments are separated by a physical barrier in which a number of micron-size grooves are embedded to allow growth of neurites across the barriers while maintaining fluidic isolation. Cells are plated into the somal (cell body) compartment and after 3-4 days, axons extend into the adjacent compartment via the grooves. We have successfully used this device to culture primary rat cortical and hippocampal neurons for upto 3 weeks. We demonstrate the ability to maintain fluidically isolated compartment and, thus, expose localized areas of neurons to insults applied in soluble form. We also use microfluidics-compatible surface micropatterning approach to facilitate identification and visualization of neurons. The ability to direct sites of neuronal attachment and orientation of axon outgrowth by micropatterning techniques, combined with fluidically isolated compartments within the culture area offer significant advantages over standard open culture methods and other conventional methods for manipulating distinct neuronal microenvironments.

4:40pm **BI-ThA9 Investigations About the Formation of Supported Phospholipid Bilayers on Structured Surfaces***, **B. Seantier**, I. Pfeiffer, M. Zaech, D. Sutherland,* Chalmers University of Technology, Sweden

There has been a strong current interest in the interaction of lipid vesicles with different homogenous materials surfaces. A number of mechanisms have been discussed leading to the formation of Supported Phospholipid Bilayers (SPBs) (for example on flat SiO@sub 2@) or intact vesicles (for example on flat Au). In our study, we have utilized lithographically defined nanoscale patterns to investigate the role of local variations in surface topography and chemistry on vesicle-surface interaction. We have studied surfaces combining two chemistries (SiO@sub 2@ and Au) where the domain sizes are similar to or below the characteristic size of the vesicles. The mechanism of the SPB formation has been studied by varying parameters such as phospholipids composition, vesicles size and concentration, and the ionic strength of the buffer solution. Quartz Crystals sensor surfaces were structured using dispersed colloidal monolayer masks (d=100nm) and lift off pattern transfer giving pits with combinations of upper and lower surface (~20% of the total surface area) chemistries. 100 nm and 200 nm extruded vesicles of POPC and DMPC have been used to form SPBs (vesicle conc. range varied between 50 µM and 500 µM with and without CaCl@sub 2@). Parallel experiments with identical surfaces utilized Quartz Crystal Microbalance with Dissipation monitoring technique and the Atomic Force Microscopy technique providing time-lapse images of the SPBs formation. The results show a two step mechanism, different from the classical SPB formation, which cannot be explained by the superposition of the vesicle behavior on Au and SiO@sub 2@ surfaces. A complex mechanism involving trapping vesicles in holes and SPB formation at the pits is assumed. In the future perspectives, the size and the shape of the Au pits will be varied. This study should allow us to better understand the influence of the surface topography and chemistry on the SPB formation.

5:00pm **BI-ThA10 Bionanodevices Integrating Biomolecular Motors***, **R. Tucker,*** University of Florida*; S. Ramachandran, D. Wu, T. Nitta,* University of Washington*; H. Hess,* University of Florida

Biomolecular motors have the ability to convert chemical energy into mechanical work with high efficiency, and can be used to integrate active movement and actuation into hybrid micro- and nanodevices. Recent improvements in the design of nanoscale transport systems (molecular shuttles) based on the motor protein kinesin will be discussed. We will focus in particular on the selective capture of target analytes by the transporters, and on improving the control over motor activation. An investigation into the origins of velocity dispersion of molecular shuttles traveling in channels permitted us to compare sample dispersion occurring in this novel mechanism of transporting samples with established transport methods, such as pressure-driven fluid flow or electroosmotic flow. Applications for biomolecular motor-based devices can be found in a variety of biosensing scenarios.

Electronic Materials and Processing
Room 309 - Session EM1-ThA

Organic and Molecular Optoelectronics

Moderator: A.V. Walker, Washington University in St. Louis

2:00pm **EM1-ThA1 Quantum Dot Light Emitting Devices for Pixelated Full Color Displays*, V. Bulovic,*** MIT **INVITED**

Quantum Dot Light Emitting Devices (QD-LEDs) developed over the past three years demonstrate high external quantum efficiencies, saturated visible color emission, narrow-band infra-red emission, and a scalable fabrication technique. This recent development is a result of advancements in the chemistry of colloidal quantum dot synthesis and demonstrations of new fabrication methods for generating thin films of QDs. The talk will present the recent technical and physical highlights, and chart the way to the next generation of the QD-LED technology.

2:40pm **EM1-ThA3 Organometallic Approaches to Achieving High Efficiency Monochromatic and White Electroluminescence from OLEDs*, M.E. Thompson,*** University of Southern California **INVITED**

There has been a great deal of interest in developing new materials for the fabrication of light emitting diodes, built from molecular and polymeric materials. A significant motivation for this work has been their potential for use in future flat panel displays. Our work has been focused on developing new emissive and charge transporting materials for these devices. Our materials have led to marked improvements in the efficiencies of these devices. In particular, we have efficiencies for LEDs close to 100%, by using phosphorescence based emitters. The phosphorescent dopants in these devices are heavy metal containing complexes (i.e. Pt, and Ir compounds). I will discuss the basic mechanism of electroluminescence in OLEDs, and then elaborate on the use of phosphorescent complexes to achieve high EL efficiencies in monochromatic OLEDs. In the discussion of electrophosphorescence I will highlight specifically how we tune emission color in both Pt and Ir based emitters by careful design of both the metal complexes and ligands. We have also demonstrated white light emitting OLEDs, using many of the same emissive materials. These devices emit simultaneously from monomer and dimer/aggregate states of Ir and Pt dopants. The result is an emission spectrum that covers the entire visible spectrum, giving true white illumination. We have recently prepared binuclear Pt complexes and can show that the low energy emissive species in the white OLEDs is most likely a ground state dimmer or aggregate. This aggregate state undergoes a structural change in the excited state, similar to an excimer. I will discuss the mechanism of electroluminescence in this system and describe our recent advances in achieving high efficiency white electroluminescence.

3:20pm **EM1-ThA5 Chemical Vapor Deposition of Thin Films of Electrically Conducting PEDOT*, J.P. Lock,*** *J.L. Lutkenhaus, N.S. Zacharia, P.T. Hammond, K.K. Gleason,* MIT

Chemical vapor deposition (CVD) technology, vital to the fabrication of traditional semiconductor devices, is also desirable for next-generation organic devices, particularly for creating layers which are difficult to process by solution methods or for coating substrates which can not tolerate exposure to solvents. In this work, a CVD process has been demonstrated for the deposition of conducting poly-3,4-ethylenedioxythiophene (PEDOT). This CVD process eliminates the need for polystyrene sulfonate (PSS), which is used to disperse PEDOT in water, but has been identified as a possible source of corrosion in OLEDs leading to shortened device lifetimes. The CVD PEDOT films range from 50 nm to several microns in thickness. Fourier transform infrared spectroscopy confirms the similarity in chemical structure of PEDOT synthesized by CVD and solution techniques. An electrical conductivity as high as 4.37 S/cm has been achieved. The CVD process utilizes a modest stage temperature and results in conformal coatings of high surface area features like fibers and pores. This combination of characteristics has allowed PEDOT deposition onto paper and fabrics to be demonstrated. Conformal coating of microporous or fibrous materials by CVD PEDOT has the potential to lead to better efficiencies in organic devices with high effective surface areas including photovoltaics. Reversible electrochromic responses of CVD PEDOT have been observed as well. The light blue films in their as-deposited state turn darker blue upon electrochemical reduction. The maximum contrast to date is 16.5% with a switching speed of 27 msec for a film having a thickness of 50 nm.

3:40pm **EM1-ThA6 Molecular Level Alignment and the Role of the Charge Neutrality Level at Organic-Organic Heterojunctions*, W. Zhao,*** Princeton University*; H. Vazquez, F. Flores,* Universidad Autonoma de Madrid, Spain*; A. Kahn,* Princeton University

The electronic structure of organic-organic (OO) interfaces is a key aspect of organic devices such as OLEDs and PV cells. Molecular level offsets at OO interfaces determine transport across devices, and directly affect their performance. This talk reports a recent investigation of the electronic structure of several OO interfaces between films of molecules such as tris(8-hydroxy-quinoline)aluminum (Alq@sub 3@), 1,4,5,8-naphthalenetetracarboxylicdianhydride (NTCDA), iridium-bis(4,6,-di-fluorophenyl-pyridinato-N,C@super 2@)-picolinate (FIrpic) or copper phthalocyanine (CuPc). The filled and empty states of these materials, their ionization energy (IE) and electron affinity (EA), and the interface molecular level alignment are determined via ultra-violet and inverse photoemission spectroscopy (UPS, IPES). Unlike many previously investigated OO heterojunctions,@footnote 1@ these are found not to follow vacuum level alignment and exhibit significant interface dipoles ranging from 0.2 to 0.5 eV. The analysis of these and previous results on OO heterojunctions is performed using the extension of the concept of charge neutrality level (CNL), developed for metal/organic interfaces,@footnote 2@ to the OO heterojunction.@footnote 3@ The energy-level alignment is driven by the alignment of the CNLs of the two organic semiconductors. The initial offset between the CNLs gives rise to a charge transfer across the interface, which induces an interface dipole and tends to align the CNLs. The initial CNL difference is reduced according to the screening factor S, a quantity related to the dielectric functions of the organic materials. Good quantitative agreement with experiment is found. This allows, for the first time, a semi-quantitative prediction of the electronic structure of OO heterojunctions. @FootnoteText@ @footnote 1@ I.G. Hill et al., Appl. Surf. Sci. 166, 354 (2000); @footnote 2@ H. Vazquez et al. EuroPhysics Lett. 65, 802 (2004); @footnote 3@ H. Vazquez et al. Phys. Rev B Rapid Comm. 71, 041306 (2005).

4:00pm **EM1-ThA7 New Device Functionalities and Materials*, N. Tessler*,** Technion, Israel Institute of Technology **INVITED**

For certain device applications, semiconducting polymers can replace inorganic semiconductors at lower cost because they are more easily processed. Examples include the development of organic light emitting diodes (OLEDs), for full color screen applications, and of the development of field effect transistors (FETs) for smart circuit applications. These device applications make use of the semiconducting nature of conjugated polymer. However, by accounting for the organic (molecular) nature of these materials one can extend the material and device functionalities. In this contribution we highlight two approaches: a) the use of nano-composites b) the use of bio-inspired chemical modifications to produce libraries of functional materials. We will also address device properties and suitable methods for analysis.

4:40pm **EM1-ThA9 Photoelectron Spectroscopy of Phenylene Ethynylene versus Phenylene Vinylene Oligomers: a Search for Bond Alternation Effects*, L.B. Picraux*,** *C.D. Zangmeister, S.W. Robey, R.D. van Zee,* NIST

Interest in factors controlling transport through conjugated molecular systems has lead to a significant experimental effort investigating conductivity in various configurations of metal-molecule junctions. One interesting result of these efforts was an investigation of the relative conductivity in junctions formed using crossed wire techniques containing phenylene ethynylene (OPE) or phenylene vinylene (OPV) oligomers. Vinylene-based oligomers were found to exhibit higher conductivity, a result that was attributed to an increased bandgap in phenylene ethynylene systems due to the larger impact of bond alternation effects in the triple bond containing system. We have used photoelectron spectroscopy to investigate the @pi@ electronic structure of these two systems, namely three-ring phenylene ethynylene oligomers with thiol bound to gold and the analogous three-ring OPV system, which were the compounds employed in the crossed-wire investigations. Spectra for the two oligomers are quite similar but the @pi@ levels in the OPV variant are approximately 0.2 eV closer to the Fermi level than in OPE, possibly consistent with the higher conductivity measured in crossed-wire junctions.@footnote 1@ While this could be construed as being consistent with a narrowing of the band gap in the OPV system, it appears to arise from a rigid shift of the levels. There is no evidence of increased dispersion within the @pi@ manifold as expected if reduced bond alternation were the cause. Finally, we will also discuss the potential impact of the self-assembled monolayer structure on transport measurements. @FootnoteText@@footnote 1@Kushmerick JG, Hold DB, Pollack SK, et al., J. Am. Chem. Soc. 124(36): 10654-10655 2002.

5:00pm **EM1-ThA10 Monomolecular Insulator Film***, **Y. Tai**, H. Noda, A. Shaporenko, M. Grunze, M. Zharnikov,* Universität Heidelberg, Germany

Progress in fabricating smaller and more efficient structures in electronic and spintronic devices depends on better dielectric materials for nanofabrication. A perspective nanoinsulator is a molecular thin organic film - self-assembled monolayer (SAM), which provide an alternative to commonly used oxide dielectrics such as e.g. SiO@sub 2@ or Al@sub 2@O@sub 3@. A so far unresolved technological problem for applications of SAMs in microelectronics and spintronics is the difficulty of fabricating stable metal layers on their surfaces, i.e. at the SAM-ambient interface. Such a film is generally leaky for metal adsorbates, which makes it impossible to integrate it into a multilayer assembly (e.g. in a tunnel junction magnetic memory cell) or to fabricate metal electrodes on its surface (e.g. in an organic thin film transistor). Using nickel as a test metal adsorbate and several different substituted and non-substituted SAMs as test substrates, we show that this difficulty can be overcome by the combination of a special design of the SAM constituents and their extensive cross-linking by low-energy electron irradiation. The properties of the SAM insulator and the metal overlayer were monitored by several complementary experimental techniques, including X-ray absorption spectroscopy and electrochemical measurements. The approach represents an important step toward the technological applications of monomolecular dielectric layers.

Electronic Materials and Processing
Room 310 - Session EM2-ThA
Dilute Nitrides and Small Bandgap Semiconductors

Moderator: R. Ahrenkiel, University of Denver

2:00pm **EM2-ThA1 Narrow Band Gap Group III-Nitrides***, **W. Walukiewicz,*** Lawrence Berkeley National Laboratory **INVITED**

Incorporation of small amounts of N into group III-V semiconductors leads to a dramatic reduction of the band gap of resulting IIIN@sub x@V@sub 1-x@ alloys. This effect can be well described by the Band Anticrossing (BAC) model that considers the interaction between localized states of N and the extended conduction band states. The interaction splits the conduction band into two nonparabolic bands, resulting in large changes in the electrical and optical properties of these materials. The BAC model provides a consistent and quantitative description of experimentally observed data including the large band gap bowing, splitting of the conduction band, and increase of the electron effective mass. Comprehensive studies of the electronic structure and electrical and optical properties of InN and In-rich In@sub 1-x@Ga@sub x@N alloys will also be discussed. In addition to having a narrow gap (0.7 eV), InN also has an extremely high electron affinity of 5.8 eV, placing the conduction band edge of this material 0.9 eV below the average energy of dangling bond defects (Fermi level stabilization energy, E@sub FS@). This unusual band alignment has profound consequences for the behavior of dopants and defects and explains the extreme proclivity of InN and In-rich group III-nitride alloys for n-type conduction. As grown, undoped InN is always n-type with electron concentrations ranging from mid 10@super 17@ cm@super -3@ to as high as 10@super 21@ cm@super -3@. We show that similar range of electron concentrations can be achieved by irradiation of thin InN films with 2 MeV He@super +@ ions.

3:00pm **EM2-ThA4 Electronic Properties of GaAsN Quantum Wells***, **S. Turcotte**, N. Shtinkov, J.-N. Beaudry,* École Polytechnique de Montréal, Canada*; G. Bentoumi,* Université de Montréal, Canada*; R.A. Masut,* École Polytechnique de Montréal, Canada*; R. Leonelli,* Université de Montréal, Canada*; P. Desjardins,* École Polytechnique de Montréal, Canada

Dilute semiconductor nitrides heterostructures are very promising for a variety of device applications including lasers and photovoltaic cells. The optimization of such devices relies on the understanding of the fundamental electronic properties of quantum well structures. Among these, optical transitions, quantum confinement, and band offsets need to be clarified. Using a combination of techniques including optical absorption and photoluminescence, we have studied GaAs@sub 1-x@N@sub x@ quantum wells in GaAs(001). Two series of samples grown by MOCVD were investigated. The first consists of 7-period, 10-nm-thick GaAs@sub 1-x@N@sub x@ multiple quantum wells (MQW) with x ranging from 0.001 to 0.02 as determined from high-resolution x-ray diffraction. A series of single quantum wells (SQW) was also fabricated to investigate the effect of well thickness, from 2.8 to 11.3 nm, for a nominal N content of x=0.01. The low-temperature (near 5K) PL spectra of the MQWs are characterized by a 10-20 meV wide emission peak at an energy decreasing from 1.5 eV to 1.3 eV with increasing N content. Annealing at 700°C for 2 min. resulted in more intense PL emission with negligible change in energy. Electronic structure calculations are carried out using a tight-binding model.@footnote 1,2@ We obtain an excellent agreement between experimental and numerical results for the case corresponding to perfectly aligned GaAs and GaAsN valence bands. The absorption edge measured at 6 K for the SQWs structures decreases from 1.45 to 1.35 eV with increasing thickness. By fitting these results to the tight-binding calculations, we deduce an electronic confinement of the order of 55 meV and 125 meV for the thickest and thinnest layers, respectively. @FootnoteText@ @footnote 1@ N. Shtinkov, P. Desjardins, and R. A. Masut, Phys. Rev. B 67, 081202(R) (2003)@footnote 2@ N. Shtinkov, S. Turcotte, J.-N. Beaudry, P. Desjardins, and R. A. Masut, J. Vac. Sci. Technol. A 22, 1606 (2004)

3:20pm **EM2-ThA5 High-Performance, Lattice-Mismatched GaInAs***, **M.W. Wanlass,*** National Renewable Energy Laboratory **INVITED**

GaInAs is a pseudobinary III-V compound semiconductor that has a direct bandgap, and full miscibility, over its entire composition range. The room-temperature bandgap varies significantly, from 0.36 eV (InAs) to 1.42 eV (GaAs), between the binary endpoints. The above characteristics make GainAs particularly well suited to photovoltaic (PV) energy converter applications that require infrared-responsive components. Arbitrary bandgaps within the available range are achieved by considering epitaxial, lattice-mismatched (LMM) heterostructures grown on commercially available crystalline substrates (e.g., Ge, GaAs, and InP). We discuss structural approaches involving compositional grading that yield LMM materials with excellent minority-carrier parameters. A variety of characterization techniques are used to elucidate the microstructural and electronic properties. Specific PV device applications and results are also presented.

4:00pm **EM2-ThA7 Comparison of a Dominant Electron Trap in n-Type and p-Type GaNAs Using Deep-Level Transient Spectroscopy***, **S.W. Johnston**, S.R. Kurtz,* National Renewable Energy Laboratory

Both p-type and n-type dilute-nitrogen GaNAs epitaxial layers grown by metal-organic chemical vapor deposition were characterized by deep-level transient spectroscopy (DLTS). For each case, the dominant DLTS signal corresponds to an electron trap having an activation energy of about 0.2 to 0.3 eV for p-type GaNAs and about 0.3 to 0.4 eV for n-type GaNAs. In p-type GaNAs, the electron traps fill slowly, as the DLTS signal reaches saturation using zero-bias filling pulses with widths on the order of 1 to 10 seconds. When applying a large range of filling-pulse widths, the activation energy tends to decrease from about 0.3 eV for short filling pulses to about 0.2 eV for longer filling pulses. In n-type GaNAs, the electron trap activation energy also tends to slightly decrease with increasing filling-pulse widths. For short pulse widths of microseconds to milliseconds, the activation energy is just below 0.4 eV, and for long pulse widths of seconds, the activation energy is just above 0.3 eV. The electron traps fill quickly in the n-type GaNAs, as the DLTS signal approaches saturation in microseconds. The capture cross-sections determined by the DLTS Arrhenius plots are typically about 10@super -13@ to 10@super -12@ cm@super 2@. The electron-trap densities range from 10@super 15@ to 10@super 16@ cm@super -3@ in mid-10@super 17@ cm@super -3@ n-type-doped GaNAs having a bandgap of 1.35 to 1.4 eV. These trap parameters give an estimated carrier lifetime of 1 ns or substantially shorter.

Magnetic Interfaces and Nanostructures
Room 204 - Session MI-ThA
Magnetic Oxides

Moderator: A. Hoffmann, Argonne National Laboratory

2:00pm **MI-ThA1 Doped Cobaltites: Phase Separation, Intergranular GMR, and Glassy Transport Phenomena***, **C. Leighton**, J. Wu,* University of Minnesota*; J. Lynn, C. Glinka,* NIST*; H. Zheng, J. Mitchell,* Argonne National Laboratory*; W. Moulton, M. Hoch, P. Kuhns, A. Reyes,* National High Magnetic Field Lab*; C. Perrey, C.B. Carter,* University of Minnesota **INVITED**

Magneto-electronic phase separation, where a chemically homogeneous material displays spatial coexistence of multiple magnetic and electronic phases, is very common in perovskite oxides and is thought to play a key role in high temperature superconductivity and colossal magnetoresistance. We have used a battery of complementary experimental techniques to tackle the problem of magnetoelectronic phase separation in the perovskite cobaltite La1-xSrxCoO3. This is a material that offers many of the desirable attributes of a model system for investigating phase separation. Co and La NMR and small angle neutron scattering unequivocally demonstrate the existence of magnetoelectronic inhomogeneity in polycrystalline, single crystal and epitaxial thin film samples, which are chemically homogeneous on nm length scales. At low doping ferromagnetic metallic clusters form in an insulating matrix. These clusters coalesce with increasing doping, leading to a percolation transition and the onset of long-range ferromagnetic order. In single crystals, this formation of isolated clusters leads to a hysteretic negative MagnetoResistance (MR), which has field, temperature, and doping dependencies consistent with an intergranular Giant MagnetoResistance (GMR) effect. We argue that this system is a naturally forming analog to the artificial structures fabricated by depositing nanoscale ferromagnetic particles in a metallic or insulating matrix, i.e. this material displays an intergranular GMR effect without the deliberate introduction of chemical interfaces. The formation of nanoscopic F clusters also gives rise to glassy transport phenomena that are reminiscent of relaxor ferroelectrics. This is discussed in terms of the known phenomenology of the magnetic phase separation. Work supported by ACS PRF and NSF MRSEC.

2:40pm **MI-ThA3 MBE Growth of Epitaxial Co@sub2@MnGe on SrTiO@sub3@ (001) and MgO (001) Substrates***, **S.K. Srivastava**[1], C. Adelmann, X. Dong,* University of Minnesota*; D. Schlom,* Penn State University*; C. Ahn,* Yale University*; C.J. Palmstrom,* University of Minnesota

The combination of metallic ferromagnetic Heusler alloys with metal oxides can be used for the formation of multifunctional material heterostructures. The growth of Co@sub2@MnGe with a 45° in-plane rotation results in a lattice mismatch of -3.84% and +3.82% for SrTiO@sub3@ (001) and MgO (001), respectively. Etching of SrTiO@sub3@, followed by ex-situ annealing in O@sub2@ (~1 atm) at 1223K for 1 hour was used to form a TiO@sub2@ terminated surface@footnote 1@ with straight edged steps. AFM shows terraces with step heights on the order of one unit cell (~ 4Å) and LEED images show a (@sr@5x@sr@5)R26.6° superstructure. The growth of Co@sub2@MnGe was initiated by growing alternating atomic layers of MnGe and Co in an MBE system at 298K to promote wetting of the substrate and the desired (001) atomic stacking sequence. Following the growth of 20 atomic layers, the film was annealed in-situ at 673K for 1 hour. The remaining 250Å Co@sub2@MnGe film was grown by codeposition at 723K and annealed at 823K for 1 hour. RHEED and LEED images from the Co@sub2@MnGe films showed (2x2) reconstruction. For growth on MgO, the substrates were cleaned and annealed ex-situ in O@sub2@ (~1 atm) at 1273K for 2 hours giving a (1x1) RHEED pattern. A growth scheme similar to the one mentioned above was used for the growth of Co@sub2@MnGe on MgO and resulted in a (2x2) RHEED pattern. XRD is consistent with the single crystal epitaxial growth of Co@sub2@MnGe films on SrTiO@sub3@ and MgO, with out-of-plane lattice parameters of 5.745Å and 5.758Å, respectively. Both films are ferromagnetic with no significant in-plane magnetic anisotropy as measured by VSM. This presentation will emphasize the effect of pre-treatment and deposition sequence on the structural and magnetic properties of Heusler alloy films grown on oxide substrates. Supported by ONR-MURI. @FootnoteText@ @footnote 1@G.Koster, B.L.Kropman, G.J.H.M.Rjinders, D.H.A.Blank and H.Rogalla, Appl. Phy. Lett., 73, 2920 (1998).

3:00pm **MI-ThA4 Characterization of Transition Metal Doped MOCVD-Grown ZnO Epifilms and Nanostructures***, **D. Hill,** R. Gateau,* Rutgers University*; J.F. Veyan,* Univ. Tech. Frederico Santa Maria*; L.S. Wielunski, S. Guha, R.A. Bartynski,* Rutgers University*; D.A. Arena,* Brookhaven National Lab*; J. Dvorak,* Montana State University*; P. Wu, Y. Lu, F. Cosandey, V. Poltavets, M. Greenblatt,* Rutgers University

ZnO is a wide bandgap (~3.3 eV) semiconductor that recently has been identified as a promising DMS candidate for room temperature spintronics. We have characterized the chemical, compositional, and magnetic properties of transition metal- (TM-) doped ZnO epitaxial thin films and nanostructures grown by MOCVD. The films and nanopillars were doped with Mn or Fe either by ion implantation or in-situ during MOCVD growth. RBS ion channeling shows a minimum yield < 2% for the ZnO epi films indicating excellent crystallinity. The minimum yield is much higher for the ion implanted samples, but improves dramatically upon annealing. Soft x-ray absorption spectroscopy (SXAS) indicates that the TM dopant may be in either the 2+ or 3+ oxidation state, depending upon annealing history. In-situ doped films exhibit oxidation states similar to ion implanted films that have been annealed. SQUID magnetometry measurements show that both the implanted and annealed films and nanostructures exhibit hysteretic M vs. H curves at temperatures as high as liquid nitrogen temperature. M(T) curves show a small paramagnetic component at 5 K, but the majority of the magnetization remains up to room temperature. TM-ion implanted MOCVD-grown ZnO nanotips show relatively uniform TM concentration (<~ 5%) throughout the tip, and TEM images show no indication of secondary phase formation or metal clustering upon annealing to temperatures as high as 700C. @FootnoteText@ @footnote 1@Supported by NSF grant # ECS-0224166 .

3:20pm **MI-ThA5 Detailed Investigation of Cr-doped Anatase TiO@sub 2@ as a Potential DMS***, **T.C. Kaspar**, T.C. Droubay, S.M. Heald, V. Shutthanandan, C.M. Wang, D.E. McCready, J.E. Jaffe, S.A. Chambers,* Pacific Northwest National Laboratory

Since the initial discovery of room temperature ferromagnetism in Co-doped anatase TiO@sub 2@ in 2001, there has been an explosion of interest in doped transition metal oxides as potential dilute magnetic semiconductors (DMSs), which may find application in future spintronic devices. The high electron mobility in n-type anatase TiO@sub 2@ (reduced to create oxygen vacancies) makes it an attractive candidate as a oxide semiconductor host material. Doping with Cr instead of Co is advantageous since Cr metal (antiferromagnetic) is more easily oxidized than Co metal (ferromagnetic). In this talk, we present results of a detailed study of Cr-doped anatase TiO@sub 2@ deposited by oxygen-plasma-assisted molecular beam epitaxy. Phase-pure, epitaxial films are obtained with particle-free surfaces and uniform distribution of Cr. Crystalline perfection is controlled by the deposition rate; nearly perfect films can be obtained at a sufficiently slow rate. For faster deposition rates, room temperature ferromagnetism is observed, with ~ 0.5 µ@sub B@/Cr and a Curie temperature of 690 K. Regardless of deposition rate, XANES and EXAFS indicate Cr incorporates into the anatase lattice as Cr(III), requiring one oxygen vacancy for every two dopants to maintain charge neutrality. The specific site occupancy, as well as the complex role of oxygen vacancies and crystalline defects in the ferromagnetic ordering, will be discussed. The electronic properties of Cr-doped anatase have been investigated in detail by XPS, XAS/XES, XMCD, and anomalous Hall measurements, as well as theoretical calculations of the band structure. These results and the implications for spintronic applications of Cr-doped anatase will be presented.

3:40pm **MI-ThA6 Structural, Electronic and Magnetic Properties of MBE Grown Ti-doped @alpha@-Fe@sub 2@O@sub 3@***, **S.A. Chambers**, T.C. Droubay, S.M. Heald, C.M. Wang, K. Rosso,* Pacific Northwest National Laboratory

@alpha@-Fe@sub 2@O@sub 3@ is an antiferromagnetic wide bandgap semiconductor (E@sub g@ = 2.2 eV) which exhibits strong ferromagnetic coupling within cation layers perpendicular to the c axis, and antiferromagnetic coupling between adjacent cation layers. LSDA + U calculations predict that substituting Ti for Fe should lead to a ferrimagnetic state with a large moment per Ti because Ti is predicted to substitute for Fe preferentially in alternating cation layers perpendicular to the c axis.@footnote 1,2@ To test this prediction, we have used oxygen plasma assisted molecular beam epitaxy to grow @alpha@-Ti@sub x@Fe@sub 2-x@O@sub 3@, for which x varied between 0.01 and 0.04, on @alpha@-Al@sub 2@O@sub 3@(0001). Excellent heteroepitaxy was achieved by first growing a @alpha@-Cr@sub 2@O@sub 3@ buffer layer to grade the lattice mismatch between @alpha@Fe@sub 2@O@sub 3@ and @alpha@-Al@sub 2@O@sub 3@. All Fe was found to be in the +3 charge state by Fe K-shell XAS and Fe 2p XPS. Ti was found to be in the +4 charge state and to uniformly substitute for Fe(III) in the lattice by Ti K-shell XAS and EXAFS, along with ion channeling. The conductivity increased monotonically with x, achieving a value of ~100 Ohm-cm at x = 0.04. All doped films were found to be weakly ferromagnetic at room temperature, as expected if Fe ions were replaced with Ti(IV) ions in a statistical fashion in all cation layers. The coercive field was found to be ~800 Oe, independent of x. The moment was found to be ~0.5 µ@sub B@ per Ti dopant, considerably lower than the 4 µ@sub B@ per Ti dopant predicted by LSDA + U theory.@footnote 1,2@. @FootnoteText@ @footnote 1@ W.H. Butler et al., J. Appl. Phys. 93, 7882 (2003).@footnote 2@ A. Bandyopadhyay et al., Phys. Rev. B 69, 174429 (2004).

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[1] **Falicov Student Award Finalist**

4:00pm **MI-ThA7 Highly Spin Polarized Current from Tunnel Spin Injectors and in Magnetic Tunnel Junctions using MgO(100)*, S.S.P. Parkin,*** IBM Almaden Research Center **INVITED**

Spin-based electronics, often referred to as "spintronics", is a research field of intense current interest, which aims to develop novel sensor, memory and logic devices by manipulating the spin states of electrons or holes in semiconducting materials. This talk will focus on electrical spin injection into semiconductors, which is a prerequisite for spintronics and, in particular, on tunnel based spin injectors operable above room temperature. Two types of spin injectors, formed from 3d transition metal ferromagnets and oxide tunnel barriers, are discussed: a three-terminal magnetic tunnel transistor (MTT) injector)@footnote 1,2@ and a two-terminal magnetic tunnel injector.@footnote 3@ A two terminal tunnel spin injector, comprised of CoFe/MgO(100), is shown to give more than 50% spin polarized current within GaAs (100) heterostructures at room temperature.@footnote 3@ The spin polarization of the injected current is inferred from the electroluminescence polarization (ELP) from GaAs/AlGaAs quantum well detectors. The high polarization values are consistent with giant values of tunneling spin polarization (TSP) measured in superconducting tunneling junctions in which the CoFe/MgO layers are highly textured (100). Recently, we have reported TSP values of up to 85% (at 0.25 K) and tunneling magnetoresistance values (TMR) of >220% in CoFe/MgO(100) magnetic tunnel junctions at room temperature.@footnote 4@ Such high values of TSP and TMR, previously only obtained at low temperatures using half-metallic ferromagnets, promise the development of new families of spintronic devices operating at room temperature based on conventional ferromagnets. * work carried out in collaboration with X. Jiang, R. Wang, C. Kaiser, R. Shelby, R. MacFarlane, G. Solomon and J. Harris. @FootnoteText@ @footnote 1@S. van Dijken et al., Appl. Phys. Lett. 83, 951 (2003). @footnote 2@ X. Jiang, et al., Phys. Rev. Lett. 90, 256603 (2003). @footnote 3@X. Jiang et al, Phys. Rev. Lett. 94, 056601 (2005). @footnote 4@S. S. P. Parkin, et al., Nature Mater. 3, 862 (2004).

Nanometer-Scale Science and Technology
Room 210 - Session NS-ThA

Nano Processing

Moderator: D.M. Tennant, Lucent

2:00pm **NS-ThA1 Control of Germanium Nanocrystal Morphology and Surface Functionalization*, H. Gerung,*** University of New Mexico*; T.J. Boyle,* Sandia National Laboratories*; C.J. Brinker, S.M. Han,* University of New Mexico

We have developed a simple synthesis route for Ge nanocrystals (Ge NCs) via reduction of Ge(II) precursor at 300 °C and 1 atm. The synthesis does not require strong reducing agents and does not produce salts or undesirable byproducts. Literature reports on Ge NC syntheses have focused mainly on direct reduction of Ge(IV) to Ge(0), which requires a combination of high temperature (>400 °C), high pressure (>1 atm), and strong reduction agents. Ge[N(SiMe@sub 3@)@sub 2@]@sub 2@ is chosen as the Ge(II) precursor due to the ease of its synthesis in high yield, the absence of potential halide contamination, and the labile amido ligand sets. The synthesis involves the injection of Ge[N(SiMe@sub 3@)@sub 2@]@sub 2@ dissolved in oleylamine into non-coordinating solvent 1-octadecene at 300 °C and 1 atm Ar. The resulting Ge NCs form quickly and show a high degree of crystallinity with no oxide formation. These NCs are mostly spherical in shape. The Ge(II) precursor's ligands can be tailored to form Ge[TMPP]@sub 2@ (TMPP = 2,2,6,6 tetramethyl piperidine) and using identical reaction conditions, cuboid Ge NCs are formed. Another alternative Ge(II) precursor, Ge[DBP]@sub 2@ (DBP = 2, 6-ditert-butylphenoxide) can be isolated from an amide alcohol metathesis reaction between Ge[N(SiMe@sub 3@)@sub 2@]@sub 2@ and 2 equivalents of DBP-H. The use of Ge[DBP]@sub 2@ under identical reaction conditions as discussed above yields Ge nanowires (Ge NWs) instead of Ge NCs. These results suggest that the Ge(II)-ligand bond strength, the steric orientation of ligands, and the subsequent surfactants formed upon decomposition of the various precursors dictate the size and morphology of Ge NCs by controlling the surface kinetics during crystal growth. We will further discuss optical and electrical characterization of Ge nanocrystals and functionalizing Ge NC surface to incorporate them into a silica matrix.

2:20pm **NS-ThA2 White Luminescence from Silica Glass Containing Nanocrystalline Silicon Prepared by RF Sputtering Technique*, K. Sato,*** *Y. Sasaki, K. Hirakuri,* Tokyo Denki University, Japan

Nanocrystalline silicon (nc-Si) is one of promising materials for application to light-related devices because it shows the particle size-depended luminescence. We previously obtained a red/green/blue luminescence from the nc-Si with various particle sizes. The white luminescence can be realized by the mixture of nc-Si which emits the red/green/blue light. In this paper, we report a fabrication technique of the silica glass containing red/green/blue luminescent nc-Si. Moreover, the luminescence property of the silica glass will be discussed. The silica glass containing nc-Si was formed by co-sputtering of Si chips/silicon dioxide (SiO@sub2@) targets and subsequently annealing at high temperature. The particle size of nc-Si was varied from 1.9 nm up to 3.0 nm by changing the deposition conditions such as radio frequency power and gas pressure in order to obtain red/green/blue luminescence from the nc-Si. The sample was evaluated by using a photoluminescence (PL) measurement. The silica glass containing nc-Si showed a broad PL spectrum with a peak at 460 nm (blue light), 550 nm (green light) and 800 nm (red light). This is due to the existence of nc-Si in which the particle size differs, i.e., the nc-Si with particle size of 1.9 nm, 2.2 nm and 3.0 nm exhibits blue, green and red luminescence, respectively. When the silica glass was irradiated by using a xenon lamp with an optical band-pass filter of 313 nm, the luminescence color from the silica glass was a white light. The white luminescence could be distinctly seen by the naked eye under room illumination.

2:40pm **NS-ThA3 Silicon Quantum Dots and Nanomembranes: Tools for Quantum Information?*, M.A. Eriksson,*** University of Wisconsin-Madison **INVITED**

Silicon has certain unusual properties, including a spin-0 nuclear isotope, that make quantum dots in this material excellent candidates for quantum information processing. Silicon can also form spectacular membranes, one hundred nanometers thick and centimeters across. Such silicon nanomembranes bend and flex like plastic sandwich wrap but retain their single crystal electronic properties. I will present results on silicon quantum dots fabricated using both Schottky gates and Atomic-Layer-Deposition MOS gates on Si/SiGe modulation-doped heterostructures. These dots have excellent charge stability, but their fabrication currently requires special processing. I also will present recent results on silicon nanomembranes, a material that retains the excellent intrinsic properties of silicon, but that can be bent, strained, and rolled into tubes. These properties offer the potential to use strain in a defect-free system, potentially leading to new ways to create quantum dots with few end-processing complexities. X-ray scattering, TEM, and low temperature electronic transport measurements will be presented, and the prospects for meaningful application of such membranes will be discussed. Work performed in collaboration with L.J. Klein, K.L.M. Lewis, K.A. Slinker, L. McGuire, Srijit Goswami, W. Peng, C. Haselby, D.W. van der Weide, R.H. Blick, S.N. Coppersmith, R. Joynt, Mark Friesen, M.M. Roberts, D. Savage, M.G. Lagally (University of Wisconsin-Madison) and J.O. Chu (IBM Watson).

3:20pm **NS-ThA5 Fabrication and Characterization of ZnO Quantum Dots and Nanosheet Structure*, R. Mu,*** Fisk University*; Y.C. Liu, H.Y. Xu, S.J. Chen,* Northeast Normal University, PRC

ZnO quantum dots and nanosheets have been fabricated via oxygen plasma assisted electron-beam deposition of ZnF2 and physical vapor transport techniques. Raman measurements of ZnO QDs showed a strong optical phonon confinement effect and the presence of surface phonon mode which does not exist in Raman spectra of ZnO films. A large blueshift in optical absorption and ultraviolet photoluminescence (UV PL) spectra were observed for ZnO QDs due to a strong quantum confinement effect of excitons. ZnO QDs posses an anomalous temperature dependent behavior in UV PL intensity. In the case of nanosheet, temperature dependent study show a surprisingly strong high temperature (857K) photon emission A brief discussion is given in an attempt to understand the physical mechanisms.

3:40pm **NS-ThA6 Induced Growth of Calcite and Gypsum using an Atomic Force Microscope@footnote 1@*, A.L. McEvoy,*** *F. Stevens, S.C. Langford, J.T. Dickinson,* Washington State University

Bond breaking at surfaces due to stimuli such as exposure to energetic radiation, mechanical stress, or chemical agents is well established. We examine the consequences of combining localized mechanical stress (due to contact with the tip of an atomic force microscope) and exposure to aqueous solutions. We show that we can induce highly localized, nanometer scale growth on single crystal surfaces of calcite (CaCO@sub

3@), an important biomineral, and gypsum (CaSO@sub 4@-2H@sub 2@O) through combined exposure to supersaturated solutions and mechanical stress. Growth occurs along step edges in single atomic layers. The growth rates depend strongly on step orientation. Tip induced deposition is shown to produce surfaces free of obvious defects, in contrast with spontaneous growth in highly supersaturated solutions (@sigma@ > 5). Experimental evidence is presented for tip-enhanced transport of ions to deposition sites. Implications concerning deposition and maintenance of atomically smooth surfaces, including mammalian joints, will be discussed. @FootnoteText@ @footnote 1@This work was supported by the National Science Foundation.

4:00pm **NS-ThA7 WCx Nanopartilces as Alternate Catalyst for NOx Reduction***, **A. Rumaiz**, S. Shah,* University of Delaware*; I. Baldytchev,* Unversity of Delaware

WCx nanoparticles were synthesized using Laser Assisted Inert Gas Condensation (LAIGC). In this process either a metal target is be ablated in the presence of a reactive gas or a compound target is used. The evaporated flux obtained by laser ablation is condensed by a circulating He gas to form WC nanoparticles. The structural properties of the samples were investigated using X-ray Diffraction (XRD) and X-ray Photo-Electron Spectroscopy (XPS). The feasibility of using nano WCx as an alternative catalyst for Pt is also addressed. A comparative study on two types of samples of WC (as prepared and carburized W) was done. The samples were used to check for the reduction of NOx in a simple reactor. The carburized W shows activity at temperatures around 400oC, while the as prepared WC shows activity at a slightly higher temperature. The stability of both the samples was studied by exposing them to a NOx environment at a fixed temperature (where the activity is appreciable) for an extended period of time. XPS and XRD confirm the formation of oxide phase after DeNOx. In order to study the nature of oxidation the DeNOx reaction was carried in a CO/O2/Hydrocarbon gas mixture. The results of these will be presented. Valence band measurements were carried out to compare at the Density of States (DOS) for WC and Pt. Theoretical calculations of the DOS were also done using Self Consistent Field approximation using the WIEN2k code.

4:20pm **NS-ThA8 Photo-Induced Decomposition of Palladium Acetate for Palladium Nanoparticle Production***, **C.E. Allmond**, A.T. Sellinger, G. Peman, J.M. Fitz-Gerald,* University of Virginia

Hydrocarbon reactions and rearrangements catalyzed by transition metals trigger chemical processes at the core of the petrochemical and polymer industries. The highly dispersed metal nanoparticles utilized for these reactions are generally prepared by reducing an aqueous solution of a noble metal salt or through the deposition of a precursor on a high surface area support followed by a further reduction step. Palladium acetate, [Pd(OAc)@sub 2@], is a widely favored metallorganic precursor for thin film processing on various substrates because it decomposes under ultraviolet irradiation. @footnote1@ @footnote2@ In this research, Pd and Pd acetate nanoparticles were deposited using a novel variation of matrix assisted pulsed laser evaporation (MAPLE). Samples were prepared by dissolving Pd(OAc)@sub 2@ into chloroform, then flash-frozen in liquid nitrogen. Deposition onto Si (100) wafers, NaCl crystals, and electron microscopy grids at room temperature was performed using a pulsed excimer laser (@lambda@ = 248 nm, 5 Hz, 25 ns FWHM) in a dynamic Ar atmosphere at 200 mTorr as a function of laser fluence and Pd metal loading. The nanoparticle sizes, distributions, and morphology of Pd and Pd acetate nanoparticles were characterized by high-resolution scanning electron microscopy (HRSEM), high-resolution transmission electron microscopy (HRTEM), X-ray energy dispersion spectroscopy (EDS), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD). @FootnoteText@ Jun-Ying Zhang, Hilmar Esrom, Ian W. Boyd (1996). "Decomposition mechanisms of thin pall@footnote 1@adium excimer UV radiation." Applied Surface Science(96-98): 399-404. @footnote 2@Zsolt Geretovszky, Ian W. Boyd. (1999). "Kinetic study of 222 nm excimer lamp induced decomposition of palladium-acetate films." Applied Surface Science(138-139): 401-407.

4:40pm **NS-ThA9 Engineering of Porous, Tin Oxide Nanoparticle Microshells for Chemical Sensor Applications***, **C.J. Martinez**, C.B. Montgomery, B. Hockey, S. Semancik,* National Institute of Standards and Technology

Advanced sensors for applications ranging from homeland security to space exploration will require performance characteristics that include high sensitivity and rapid response. We have sought to enhance the sensitivity and speed of conductometric gas microsensors through the design and fabrication of porous, three-dimensional tin oxide nanoparticle (@td 10@ nm) films. These films were fabricated via the self-assembly from solution of nanoparticle-decorated latex microspheres, which serve as sacrificial templates. Through heating (10@super 4@ @super o@C/sec), the latex microspheres were removed to reveal a multiscale porous 3-dimensional structure composed of interconnected hollow nanoparticle microshells with ultra-thin walls (@td 50@ nm). The multiscale porous architecture promotes analyte diffusion and maximizes available active surface area. Sensor measurements were performed by depositing these films onto MEMS microsensor platforms with inter-digitated electrodes and embedded heaters. We report on film conductance changes measured at different temperatures (300@super o@C to 450@super o@C), caused by exposure to test gases at concentrations @td 100@ ppb in a dry air background. An enhancement in sensitivity to CO, H@sub 2@O and MeOH was observed for these nanoparticle microshell films when direct comparisons were made to other nanostructured sensing films. Special attention has been given to understanding the influence that structural factors (film thickness, packing density, microshell diameter and microshell thickness) have on the sensitivity, selectivity, stability and response time of these materials.

5:00pm **NS-ThA10 Measurement of the Young's Moduli of Individual Electrospun Nanofibers***, **L.M. Bellan**,* Cornell University*; J. Kameoka,* Texas A&M University*; H.G. Craighead,* Cornell University

Our measurements of the Young's moduli of individual electrospun polymer nanofibers support previous claims that electrospinning can produce polymer fibers with high degrees of molecular orientation. Electrospinning is a technique for fabricating micro- and nanoscale fibers using a strong electric field to extract a jet from a viscous solution. These fibers may be oriented by depositing them on a rotating substrate. We have used this technique to deposit oriented polyethylene oxide and silica glass nanofibers over trenches etched in silicon. The suspended fibers were depressed using an atomic force microscope, and the resulting force-displacement data was used to determine the Young's moduli of the individual fibers. The Young's moduli of the polyethylene oxide fibers were significantly larger than the reported values for polyethylene oxide bulk and films, which supports previous claims of molecular orientation in the fibers. The Young's moduli of the glass fibers were consistent with values calculated from previously measured mechanical resonance frequencies of similar fibers. We are currently investigating mechanical properties of individual nanofibers spun from other polymers.

Plasma Science and Technology
Room 302 - Session PS+TF-ThA

Emerging Plasma Applications

Moderator: H. Barankova, Uppsala University, Sweden

2:00pm **PS+TF-ThA1 Emerging Plasma Deposition Applications***, **D.P. Monaghan**,* Gencoa, UK **INVITED**

Vacuum plasma deposition has been the mainstay of the thin film industry since its inception. In particular magnetron sputter based processes have come to the forefront due to the inherent stability and scalability of the technique. However, the method has to constantly re-invent itself in order to provide better solution for the ever-changing world of micro-electronics and consumer products. New generations of products are also being created that rely partly or completely on new sputter based processes. This in turn can require radical changes to the usual production methods. The presentation will highlight the state-of-the art in sputter technology and in particular a number of areas that will drive further market expansion and technical advancement in the field. Some examples will include thin film batteries where virtually every feature relies upon sputtered layers of a low or high tech. nature. Due to the miniature and highly efficient nature of the product, it opens up the possibility of providing "power" to many new product classes and new devices. Thin film solar cells that have the ability to create efficient conversion of energy via a low cost and lightweight structure may lead to a reduction of societies dependence upon fossil fuels. The introduction of vertical magnetic recording comes ever closer if longitudinal recording is limited to <200 Gbit/in2. Vertical recording can potentially achieve terabyte recording density, but places much higher demands on the process equipment and magnetron source technology. Another high growth area is display technology. The emergence of high definition large area LCD displays puts a corresponding demand upon the digital video disk storage capacity. New disk formats such have Blu-ray have been shown to offer up to 3x the storage capacity. In addition the possibility of a high and low video formats on a single disk means the creation of two separate recording media in a single production process.

2:40pm **PS+TF-ThA3 Investigating the Plasma-Propellant Interaction through Experimental Modeling***, **R. Valliere**, R. Blumenthal,* Auburn University

There has been a significant interest in the use of plasmas to ignite propellants in large bore artillery. A short, reproducible ignition delay and a reduced temperature dependence are the most important advantages of plasma ignition over conventional ignition. Using the experimental modeling method, pioneered by Winters and Coburn,@footnote 1@ the erosion rates of sprayed-on films of RDX and HMX have been investigated in inert and reactive plasmas, as a function of sample bias in order to isolate the ion and electron bombardment and chemical effects on the erosion rate. No significant erosion rate was observed in argon plasmas with zero or positive bias, indicating that erosion by electron bombardment alone is not significant. Under ion bombardment conditions, large negative bias, only a slow erosion rate (presumably due to sputtering) was observed. Erosion in hydrogen plasmas is quite different. The minimum erosion rate, observed at positive and zero sample biases, was ~100x the maximum rate observed in negative-biased argon plasmas. Under negative bias the erosion rate increased as a much as 20-fold, depending on a combination of ion current and sample bias. All observed erosion rates obey pseudo-first order kinetics. The fact that the erosion rates in the hydrogen plasmas are all much greater than the rates of the argon plasmas, even at large negative bias, indicates a strong chemical component to the erosion process. The bias and current dependence of the erosion rate in hydrogen plasmas indicate a synergistic effect between ions and reactive neutrals. The kinetics of erosion for the individual species and the synergistic effects between them will be presented. @FootnoteText@ @footnote 1@ H.F. Winters, and J.W. Coburn, JVSTB @bold 3(5)@, 1376 (1985).

3:00pm **PS+TF-ThA4 PECVD of SiO@sub 2@ Thin Film from Electron-Beam Generated Plasmas***, **D. Leonhardt**, S.G. Walton,* US Naval Research Laboratory

The deposition of thin films of SiO@sub 2@ is an integral part of flexible displays/electronics, medical implant bio-functionalization, as well as a robust barrier layer ideal for space applications. In all of these applications, the SiO@sub 2@ layer must be uniform and defect free over large areas. Typical plasma-based deposition technologies that are presently used have limitations in both the quality of material being deposited and the uniformity over large (square meter) areas. NRL has used electron beam-generated plasmas to produce a variety of SiO@sub x@ films, with the focus on PECVD processes for temperature sensitive substrates that are scalable to large areas. Mixtures of TEOS or HMDSO with Ar/O@sub 2@ based plasmas were used to grow films in modulated electron beam generated plasmas. The inherent low electron temperature of these plasmas results in low plasma fields and potentials, which in turn provide low energy (< 3 eV) ions to the substrate. The resultant film electrical, optical and chemical properties with respect to gas mixtures, substrate temperature and ion energy will be presented. The low ion energies were critical in producing films with lower defect densities than typical SiO@sub 2@ deposition processes. Using the ion energy as an additional process control 'knob' the film composition ranged from stoichiometric SiO@sub 2@ to heavily hydrolyzed. Fluxes to the substrate determined by mass spectrometry measurements will be correlated to these process variables and final film composition. Along with a highly tunable PECVD process, these plasmas offer tremendous scaling and uniformity capabilities that will also be discussed.

3:20pm **PS+TF-ThA5 Nanoparticles and Nanocoatings from Plasmas: Old Problems with a New Twist***, **K.P. Giapis**,* California Institute of Technology **INVITED**

The formation of particles in processing plasmas has generally been related to contamination and lower yields and is considered undesirable. However, nanometer-size particles can have unusual properties, very different from those of bulk materials, which makes them attractive for nanotechnology applications. We have explored the formation of Si nanoparticles in continuous-flow atmospheric-pressure dc microdischarges confined in capillary tubes. The intensity and size of these discharges permits the rapid decomposition of silane, leading to nucleation and growth of 1-3 nm Si particles, whose growth is abruptly terminated as they exit the microreactor. Narrow size distributions are obtained as inferred from classification and imaging. Particles of both charge polarities are detected with similar size distribution but 2X more positively charged particles. As-grown Si particles luminesce in the blue (420nm) with a quantum efficiency of 30% and may find applications in imaging and Si-based optoelectronics. The microdischarge synthesis route is generic to any gas-phase precursor and has been also used to grow Ge and Fe nanoparticles of 1-3 nm in size in benchtop setups. Nanowires and nanotubes are promising as nanoprobes, provided they can be coated with insulating materials followed up by tip end exposure and functionalization. We have used inductively-coupled plasmas to deposit conformal fluorocarbon coatings of a few nm thickness on carbon nanotubes. The coatings provide good insulation while they improve the rigidity of the nanotubes for surface imaging. We will present results from probe immersion experiments in Hg and water. Plasmas provide a versatile way to deposit a wide variety of extremely thin coatings to enable passivation, isolation, or functionalization at the nanoscale.

4:00pm **PS+TF-ThA7 Effect of Substrate Material on Properties of TiN Films Deposited in the Hybrid Plasma Reactor***, **L. Bardos**, H. Barankova, L.-E. Gustavsson,* Uppsala University, Sweden

Parameters of TiN films deposited in the hybrid hollow cathode and microwave ECR plasma reactor can be strongly affected by the substrate material. Differences have been found between films grown on Si substrates and steel substrates, as well as between steel substrates from martensite and austenite steels. Temperature measurements by simple probes made from different materials with surfaces covered by wafers from Si or from steel confirmed substantial differences depending on individual materials. These differences can be explained by material-dependent absorptions of the microwave power as well as by enhanced particle bombardment of ferromagnetic substrates connected with deformation of the magnetic field in the hybrid plasma reactor. The effect of surface bombardment has been confirmed by voltage current measurements using electrically biased probes. The results correspond well with properties of the obtained TiN films. Observed effects could be of more general importance, e.g. for microwave ECR plasmas, magnetron sputtering as well as for most magnetized plasma systems.

4:20pm **PS+TF-ThA8 Synthesis of Aligned Carbon Nanotubes by RF-Plasma-Assisted DC Plasma Chemical Vapor Deposition***, **Y. Hayashi**, T. Fukumura,* Kyoto Institute of Technology, Japan*; R. Utsunomiya,* Nissin Electric Co. Ltd., Japan

Aligned carbon nanotubes (CNTs) grown on a substrate are expected to be applied to the electron emitters of a field emission display. Plasma-enhanced chemical vapor deposition (plasma CVD) enables highly aligned growth of multi-walled CNTs by drawing them toward plasma in the sheath electric field.@footnote 1@ However the problem of aligned CNT growth by plasma CVD is large-area growth. We have developed a new method of large-area growth of CNTs under stable DC plasma sustainment without arcing by the assistance of RF plasma. Plates of RF electrode, a grounded electrode, and DC cathode were placed parallel in this order in a vacuum chamber. The grounded electrode was gridded so as to pass a part of the RF generated plasma into the space of DC discharge. Iron substrates were placed on the cathode electrode. 13.56 MHz RF power of 500 W was induced to the RF electrode and negative bias of 325 V was induced to the cathode electrode. 20 % methane diluted in hydrogen was introduced into the chamber with the operating pressure of 1000 Pa during the growth of CNTs. Well-aligned carbon fibers were observed by scanning electron microscopy and about 50 concentric layers of graphite with hollows were observed by transmission electron microscopy. These results confirm that CNTs can be synthesized by this method. DC discharge current was 0.7 A at the discharge voltage of 325 V under the assistance of 500 W RF-plasma, while it was 0.57 A without RF-plasma. The decrease of discharge impedance caused the stable sustainment of DC glow discharge without arcing. It is concluded that the large-area growth of well-aligned CNTs under the stable sustainment of DC glow discharge can be carried out by RF-Plasma-Assisted DC Plasma CVD. @FootnoteText@ @footnote 1@Y. Hayashi, T. Negishi and S. Nishino, J. Vac. Sci. Technol. A19, 1796(2001).

4:40pm **PS+TF-ThA9 In Situ Oxidation and Plasma Studies for Magnetic Tunnel Junctions: The Mechanism of Plasma Oxidation of Ultra-Thin Aluminum Films Unraveled***, **M.C.M. Van De Sanden**,* Eindhoven University of Technology, The Netherlands*; K. Knechten,* Oce Technology, The Netherlands*; B. Koopmans, H.J.M. Swagten, W.J.M. de Jonge,* Eindhoven University of Technology, The Netherlands

Plasma oxidation of thin aluminum films is a commonly used technique to form thin aluminum oxide barriers for application in magnetic tunnel junctions (typically 1 nm). In this technique a glow discharge in oxygen (P = 5-12 W, p = 5-40 Pa) is used to oxidize ultra thin sputtered aluminum films. In comparison with thermal oxidation the process is faster and provides high values of tunneling magnetoresistance (TMR) but at the cost of higher resistance-area products (RxA). However, whereas thermal oxidation of thin aluminum films is well understood in terms of the original model of Cabrera, where the oxidation rate is limited by field-assisted thermal 'hops' of aluminum ions into the oxide, the detailed mechanism of plasma oxidation of thin aluminum films is still unknown. To unravel the mechanism in situ measurements of the oxidation rate and plasma parameters such as the ion and oxygen density are performed. The oxidation rate is determined from single wavelength ellipsometry. From these measurements we have concluded that not one single particle in the plasma is responsible for the increase in oxidation rate observed. A clear correlation of the oxidation rate with the ion flux towards the sample is observed. In addition the oxidation rate is also correlated with the atomic oxygen density in the gas. These results can be explained within a modified Cabrera model of oxidation in which the oxidation temperature is locally enhanced due to the thermal spike of an impinging ion. Additionally, due to the presence of atomic oxygen in the plasma, the field over the oxide during oxidation is enhanced by the increased adsorption of atomic oxygen on the oxide surface. Including both effects in an adjusted equation for the oxidation rate provides a good agreement between model and experiments. The model provides new insights into plasma based oxidation of ultra thin films and offers oppertunities to further control the quality of the tunnel barrier.

5:00pm **PS+TF-ThA10 High Density Plasma Processing of Si Nanocrystal Embedded SiO@sub x@ Thin Films***, **P.C. Joshi,*** SHARP Labs of America, Inc., US*; T.K. Li, W. Gao, Y. Ono, A.T. Voutsas, J.W. Hartzell, S.T. Hsu,* SHARP Labs of America, Inc.

The optical properties of Si nanocrystals are of interest for efficient and low cost integrated optoelectronic applications. The fabrication of novel optoelectronic devices, exploiting the unique optical properties of Si nanocrystals, requires thin films with high PL/EL quantum efficiency. One approach that is being actively pursued for optoelectronic devices is the fabrication of Si nanocrystal embedded SiO@sub x@ thin films. The development of stable and reliable optical devices requires thin films with high concentration and uniform distribution of Si nanocrystals with controlled particle size. In this paper, we report on the high-density plasma processing of Si nanocrystal embedded SiO@sub x@ thin films. The high-density plasma technique is characterized by low plasma potential, high plasma density, and independent control of plasma energy and density; which provide unique process possibilities and control. The high plasma concentration and low plasma potential of the HDP process are attractive for the generation of Si nanocrystals while minimizing the plasma induced bulk and interfacial damage. We have been successful in controlling the optical properties SiO@sub x@ thin films and the wavelength of the emitted PL signal over a wide range exploiting the unique characteristics of the high-density PECVD technique. The present paper describes a correlation between the optical properties and the PL characteristics of the SiO@sub x@ thin films deposited in the temperature range of 25-300 °C. The high-density plasma deposited SiO@sub x@ films have shown PL signal even in the as-deposited state while subsequent annealing (900-1100 °C) has resulted in significant enhancement of the PL intensity. The present results demonstrate the potential of the high-density PECVD technique for the low temperature processing of the Si nanocrystal embedded SiO@sub x@ thin films with controlled physical and optical characteristics for novel optoelectronic applications.

Plasma Science and Technology
Room 304 - Session PS-ThA

Plasma Sources and Equipment

Moderator: G.F. Franz, Munich University of Applied Sciences, Germany

2:00pm **PS-ThA1 Characteristics of Large-diameter Plasma using a Radial Line Slot Antenna***, **C. Tian**, T. Nozawa, K. Ishibasi, H. Kameyama, T. Morimoto,* Tokyo Electron LTD., Japan

A radial line slot antenna (RLSA) for surface-wave-plasma at 2.45GHz is a promising candidate with respect to increased process requirements for the large-diameter plasma as well as the gas dissociation control and free plasma damage. Characteristics of such a kind of plasma have been studied by both direct plasma probe measurements and numerical simulations. The discharge chamber is 40 cm in diameter and 30 cm in depth with a quartz glass window 3 cm thick on the top. A custom inductively coupled plasma (ICP) is also evaluated for comparison by replacing the RLSA with an RF coil mounted on the top window. Some unique characteristics of RLSA has been found by both radial and vertical direction plasma measurements, which are: (1) the electron temperature of RLSA is about 0.9eV-1.2eV low under the various power input and gas pressure conditions, half as many as the ICPs; (2) the main plasma generation area of RLSA is limited in the plasma surface just below the quartz glass window, while the ICP involve a much wider range; (3) the electron energy distribution functions (EEDFs) of RLSA plasma show few high energy electrons existing in the plasma diffusion area as compare to the ICPs. Numerical simulations are implemented to reveal the more essential difference in plasma generation between the RLSA and the ICP, where the superiority of RLSA plasma has been confirmed. The critical uniformity of the radial plasma distribution has been evaluated by the view of RLSA optimization. Optimal design of the slot pattern and the top glass window shape are effective in keeping the high plasma uniformity robustly from various processing conditions. Numerical analysis of microwave propagation helps to achieve the RLSA optimal design. The features of high plasma uniformity and low electron temperature lead to free plasma damage in our associated etching process.

2:20pm **PS-ThA2 Application of the Shaped Electrode Technique to a Large Area Rectangular Capacitively-Coupled Plasma Reactor to Suppress Standing Wave Non-Uniformity***, **L. Sansonnens,*** Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland*; C. Ellert, A. Buechel,* UNAXIS-Balzers AG, Liechtenstein*; H. Schmidt, A.A. Howling, C. Hollenstein,* EPFL, Switzerland

The use of VHF (very high frequency) instead of the standard 13.56 MHz excitation frequency in capacitively-coupled plasma reactors has been shown to be a promising technique for plasma-enhanced chemical vapor deposition of thin films such as amorphous or microcrystalline silicon used for the production of photovoltaic solar cells or thin film transistors for flat screens. In particular, the use of VHF has been shown to increase the deposition rate and to reduce the sheath voltage and maximum ion energy bombardment at constant plasma power. Both effects favor deposition at higher rates without degrading the thin film electronic properties. However, these advantages have generally been demonstrated in small area plasma reactors, and it has been shown that electromagnetic standing wave effects becomes the main source of non-uniformity limiting the use of VHF in large area reactors exceeding 1 m@super 2@ required for industrial applications. Recently, it has been proposed to use a shaped electrode (together with a thin dielectric plate in order to confine the plasma in a constant interelectrode gap) in place of the conventional flat electrode in order to suppress the standing wave non-uniformity. In this work, the application of the shaped electrode technique for standing wave suppression in a large area rectangular industrial reactor (substrate area: 1.1 m x 1.25 m) will be presented. In particular, film thickness uniformities for amorphous silicon deposited with and without shaped electrode at an excitation frequency of 41 MHz will be compared, and some of the implementation difficulties of the shaped electrode technique for industrial processes will be discussed.

2:40pm **PS-ThA3 Characteristics of Internal Linear Inductively Coupled Plasma and Its Etching Properties for Flat Panel Display Applications***, **G.Y. Yeom**, K.N. Kim, C.K. Oh,* Sungkyunkwan University, Korea **INVITED**

The increase of substrate size and the requirement of high rate processing for both microelectronics and flat panel display industry require large-area high density plasma sources. Among the various high density plasma sources, inductively coupled plasma sources are preferred due to its simple physics and scalability. However, conventional spiral-type external inductively coupled plasma sources can not be easily applied to the flat panel display processing due to the standing wave effect, increased capacitive coupling, etc. In this study, characteristics of an internal linear inductively plasma source was investigated as a possible high density plasma source for the application to flat panel display processing larger than 7th generation of TFT-LCD substrates. By varying the arrangements of the antenna arrays, the uniformity of the plasma has changed significantly, and, by optimizing the antenna arrangement, the plasma uniformity of 4% with the plasma density higher than 2x10@super11@ /cm@super3@ could be obtained on the substrate. Electrical characteristics of the plasma source measured by an impedance analyzer showed the low impedance and high power transfer efficiency for the optimized antenna arrangement.

3:20pm **PS-ThA5 Investigation of Frequency and Magnetic Field Effect on Single and Multiple Frequencies Capacitively Coupled Plasma Reactors***, **T. Panagopoulos**, A.M. Paterson, J.P. Holland,* Applied Materials Inc.

The effect of driving frequency and magnetic field has been investigated for a 300 mm MERIE reactor for an argon discharge using the HPEM hybrid-fluid computational model. The driving frequency varied from 2 MHz up to 200 MHz for either single or multiple frequency operation, while the magnetic field range was 0 to 225 G. Pressure was maintained low, at 30 mTorr, where the magnetic field has the most dominant effect and the power was held constant at 400 W. As the magnetic field increases the dc bias becomes less negative and the difference between plasma potential and dc bias is reduced and becomes minimal at high values of magnetic field. For low driving frequencies, up to 20 MHz, the dc bias increases (becomes more negative) with a small increase in magnetic field (40 MHz), the dc bias becomes less negative monotonically with the B field intensity. For high magnetic field (~170 G), the frequency effect on dc bias is rather weak. The electron temperature at reactor centerline decreases with increasing frequency and increasing magnetic field intensity, while the argon metastable and argon density follow opposite trends with one another at the same location. The plasma density increases with the frequency and magnetic field, while the argon metastable density peaks at low B field initially and then decreases at higher B field. The plasma potential decreases both with increasing magnetic field and driving frequency. At higher frequencies (>20 MHz) and values of magnetic field greater than 50 G, the plasma potential increases with the magnetic field and saturates at values around 200 G. Experimental results using langmuir and V-I probes confirm the trends observed in the simulation study.

3:40pm **PS-ThA6 Independent Control of Backscattering Energy and Sputter Rate in a VHF-DC Superimposed Magnetron Source***, **H. Toyoda**, Y. Sakashita, Y. Takagi, K. Sasaki, J. Gao, T. Kato, S. Iwata, S. Tsunashima, H. Sugai,* Nagoya University, Japan

Recent application of magnetron plasma to nano-scale thin film deposition requires damage-free atomic-scale flat surfaces of the deposited film. In general, surface qualities of sputter deposited films are influenced by the incidence of particles with high kinetic energies. Thus, control of energetic ions and neutrals impinging on substrate is an important issue, in order to clarify a correlation between energetic particles and film qualities. In the magnetron discharge in argon gas, a significant amount of energetic Ar atoms is backscattered from the target surface and incident on the substrate. The backscattering energy can be reduced by lowering the target voltage, but it results in a decrease in the sputter deposition rate. In this study, we present independent control of the backscattering energy and the sputter deposition rate by superimposing VHF and DC voltage to the target. Discharge characteristic and sputter deposition rate are investigated by a Langmuir probe, a quadrupole mass spectrometer (QMS) with an energy analyzer and a quartz crystal microbalance. From the QMS measurement of energetic Ar ions, a decrease in the energy of backscattered Ar atoms is inferred. It is confirmed that the sputter deposition rate of the VHF-DC superimposed magnetron discharge at lower target DC voltage (~100 V) is almost comparable to that of the conventional DC magnetron discharge at higher target voltages (>400 V).

4:00pm **PS-ThA7 Extraction of a Directional, Nearly Mono-energetic Ion Beam Using an Inductively Coupled Pulsed Plasma with an Internal Coil***, **L. Xu**, D.J. Economou, V.M. Donnelly, P. Ruchhoeft,* University of Houston

Ion beams with narrow energy and angular distributions are important for large-area sub-10 nm feature etching and deposition. In this work, a 13.56 MHz pulsed (typically 100µs ON/100µs OFF) inductively coupled plasma reactor with a two-turn nickel coil immersed in the plasma was developed to generate a nearly mono-energetic, directional ion beam. This beam may be used for etching (Ar@super +@ ions on silicon exposed to chlorine) or deposition (low energy Ni@super +@ ions on silicon). The plasma chamber was separated from the differentially pumped processing chamber by an ion drift region. A three-grid ion energy analyzer located in the processing chamber, 75 cm from the ion source, was employed to measure the ion energy distribution (IED) and ion current density. A positive voltage pulse synchronized with the power-OFF (afterglow) period of the pulsed discharge was applied to an extraction ring electrode surrounding the plasma, raising the plasma potential (V@sub p@) and "pushing" positive ions out of the plasma through a grounded grid. With 100 V applied to the extraction ring electrode during the afterglow, the energy of the extracted ion beam peaked at 100.5 eV, and the FWHM of the IED was 3.0 eV. The corresponding ion current (measured by the analyzer with 1 degree acceptance angle) was 20 times higher than the ion current extracted during the power-ON (active glow, no acceleration voltage) period. This is because ions exiting the plasma during the afterglow have a lower divergence angle, due to the vertical acceleration and low T@sub e@. The ion drift tube downstream of the plasma was found to be a "natural filter" to effectively screen out ions in the wings of the energy and angular distributions, allowing a directional and nearly mono-energetic ion beam to reach the sample. This work was supported by the National Science Foundation (NSF-NIRT-0303790).

4:20pm **PS-ThA8 Ion Energy Selection in Expanding Thermal Plasmas by Means of Pulse-Shaped Substrate Bias***, **M.A. Blauw**, A.H.M. Smets, M. Creatore, M.C.M. Van De Sanden,* Eindhoven University of Technology, The Netherlands

Pulse-shaped substrate bias was applied to the expanding thermal plasma. In contrast to a sinusoidal RF-waveform, a pulse-shaped RF-waveform can result in a mono-energetic ion flux to the substrate at much lower frequencies.@footnote 1@ A nearly constant substrate potential was observed between two consecutive pulses for argon-hydrogen and argon-oxygen gas mixtures. It implies that the ion flux is nearly mono-energetic because the plasma sheath transit time is much shorter than the pulse period. The ions that reach the substrate during the pulse have energy comparable to the ions at floating potential so that they do not influence the surface processes significantly. All details of the observed substrate potential can be fully described with the equivalent circuit diagram of the substrate bias system. Besides, the ion current density was derived from the linear voltage increase over the coupling capacitor between two consecutive pulses. The absolute ion density was calculated from the measured ion current density using the electron temperature of the bulk plasma. In contrast to a 13.56 MHz sinusoidal substrate bias, which creates a bright glow around the substrate, the pulse-shaped substrate bias does not influence the plasma visibly. The pulse-shaped substrate bias is particularly suitable to improve the properties of several plasma-deposited materials. The reason is that a mild ion bombardment enhances the rearrangement of surface atoms into an ordered structure, whereas highly energetic ions cause permanent damage.@footnote 2@ For example, the pulse-shaped substrate bias could be used to reduce the defect density in amorphous silicon, to increase the compactness of silicon oxide films on polymers, and, to improve the hardness of diamond-like carbon coatings. @FootnoteText@ @footnote 1@S.B. Wang and A.E. Wendt, J. Appl. Phys. 88, 643 +(2000). @footnote 2@J.W. Rabalais et al., Phys. Rev. B 53, 10781 (1996).

4:40pm **PS-ThA9 A Toroidal Plasma Source for Generation of High Throughput, Low Contamination Atomic Gases***, **X. Chen**, W.M. Holber, P. Loomis, J. Gunn, S.Q. Shao,* MKS Instruments, Inc.

A high power, low-field toroidal RF plasma source has been developed for generation of activated gases, such as O, H, N and F. In the plasma source, RF power is coupled through ferrite cores into the plasma that acts as a secondary of an RF transformer and is confined within a toroidal quartz chamber. A combination of toroidal plasma geometry, a quartz plasma chamber, and extremely low electric field (<8 V/cm) minimizes chamber surface erosion and associated contamination. More than twice as much of atomic oxygen is generated as compared with the current generation of remote plasma sources, resulting in 2-3 times increase in throughput for photoresist stripping. Other applications include gate dielectric modification, atomic layer deposition, annealing, and wafer cleaning. This paper characterizes the plasma source and its operation with O@sub 2@, N@sub 2@, H@sub 2@, H@sub 2@O, H@sub 2@/N@sub 2@ and H@sub 2@/He gasses. Experimental measurements of plasma density and atomic gas flux of O, N, and H, using Langmuir probes, recombination probes and calorimetry, are presented. Typical plasma density is in the order of 10@super 13@ cm@super -3@. Transport of the charged species and activated neutral species through quartz and sapphire ducts, materials commonly used as liners in semiconductor process chambers, are also reported.

5:00pm **PS-ThA10 Characterization and Modeling of a Transformer-Coupled Toroidal Plasma Source for Remote Chamber Cleaning***, **B. Bai**, J.J. An, H.H. Sawin,* M. I. T.

The transformer-coupled toroidal plasma source is widely used for remote cleaning of Chemical Vapor Deposition(CVD) chamber, in which fluorine containing gases are dissociated to form fluorine atoms for downstream etching. It was found that with the addition of a small amount of N2(0.5% of the total flow) into the fluorocarbon plasmas(C2F6 or C4F8), the etching rate of silicon dioxide film was doubled, making the etching rate comparable to NF3 plasmas under the same conditions. The increase of etching rate of silicon dioxide when N is added is due to the surface modification of the transfer tube between the source and downstream chamber, where N atoms or N containing radicals block the recombination site to form COF2 and favors the formation of CO2 thereby causing more fluorine atoms to be delivered to the downstream chamber. The toroidal plasma source was experimentally characterized. Rovibrational bands of N2 and C2 were fitted to obtain the neutral gas temperatures for NF3 and C2F6 plasmas, and they were found to be in the range of 3000-6000K, which is consistent with the high power density(>15W/cm3) coupled into the plasmas. The electron temperatures were found to be 1-4 eV, as determined by the line ratios of atomic argon spectrum. The concentrations of fluorine and oxygen atoms in the plasma source were measured by the actinometry technique and other species were detected by both the Mass Spectrometer and the FTIR. It was found that NF3, C2F6, C4F8 all had nearly 100% dissociation while CF4 had only about 50% dissociation, which makes CF4 unfavorable for the remote cleaning. Global and 1-D models were set up to simulate the toroidal plasma source as an infinite cylindrically symmetrical DC positive column. Detailed plasma chemistries were considered and first three moments of the Boltzmann's equations were applied to decide the equilibrium condition of the plasmas. The model was found to explain the experimental trend very well.

Surface Science
Room 202 - Session SS1-ThA
Transport and Structural Stabilization of Surfaces

Moderator: L. Bartels, University of California at Riverside

2:00pm **SS1-ThA1 Living on the Edge: Life and Death of Vacancies in Cu(100)***, **K. Schoots**, M.J. Rost, J.W.M. Frenken,* Leiden University, The Netherlands

We have used STM to investigate where surface vacancies originate and annihilate on Cu(100). Because of the extremely high mobility of the surface vacancies, we have been forced to use tracer particles to follow the vacancy motion, in the form of In atoms, incorporated in the top layer. The "slide-puzzle"- diffusion of the vacancies makes the In atoms move through the surface, as has been reported in.@footnote 1-3@ In the present study, we have employed tailor-made geometries, in which the In atoms were surrounded exclusively by upward or by downward steps. Our STM movies show a striking difference between these two cases, with differences in jump frequencies and average jump lenghts of more than one order of magnitude. These results show that vacancies are primarily created at the upper side of a step and can be formulated in analogy with the energetics of ad-atoms, in terms of an Ehrlich-Schwoebel barrier@footnote 4@ for surface vacancies. @FootnoteText@ @footnote 1@ R. van Gastel et al., Nature 408 (2000) 665, Phys. Rev. Lett. 86 (2001) 1562, Surf. Sci 521 (2002) 10, Surf. Sci. 521 (2002) 26.@footnote 2@ M.L. Grant et al., Phys. Rev. Lett. 86 (2001) 4588.@footnote 3@ R. van Gastel et al., The Chemical Physics of Solid Surfaces, vol. 11, Surface Dynamics, ed. D.P. Woodruff, (Elsevier, Amsterdam, 2003), p. 351-370.@footnote 4@ G. Ehrlich et al., J. Chem. Phys. 44 (1966) 1039.

2:20pm **SS1-ThA2 Diffusion of Two Dimensional Cu Adatom Islands on Cu(111) using a "Self Learning" Kinetic Monte Carlo Technique***, **T.S. Rahman**,* Kansas State University*; O. Trushin,* Russian Academy of Sciences*; A. Kara, A. Karim,* Kansas State University*; P. Vikulov,* Russian Academy of Sciences

Diffusion of two dimensional Cu adatom islands, containing 1 to 100 atoms, on Cu (111) has been studied using a newly developed "self learning" Kinetic Monte Carlo (SLKMC) technique in which the standard KMC method is combined with procedures for automatic generation of a table of microscopic events and calculation of their activation energy barriers. Nontrivial paths thus revealed and fully characterized are permanently recorded in a database for future usage, through a pattern recognition scheme. The system thus automatically builds all possible single and multiple atom processes that it needs for sustained simulation and evolves according to processes of its choosing. The diffusion coefficients calculated for 300K, 500K, and 700K, show that the effective diffusion barriers increase almost monotonically with increasing island size. From the tabulated frequencies of events we find that concerted motion and multiple particle processes play a key role in the diffusion of small islands, however, periphery diffusion and single particle processes dominate for the larger sized islands. Contrary to the case of small Cu islands on Cu (100), we do not find any oscillatory behavior for the effective diffusion barrier or for the diffusion coefficients as a function of island size.

2:40pm **SS1-ThA3 Exclusively Linear Diffusion of 9,10-Dithioanthracene on an Isotropic Cu(111) Surface***, K.-Y. Kwon, K.L. Wong, G. Pawin, **L. Bartels**,* University of California at Riverside

One-dimensional diffusion of adsorbates is a common feature of anisotropic surfaces such as the (110) and (211) cuts of an fcc crystal. The technologically-relevant lowest energy (111) surfaces of coinage metals have sixfold symmetry in the top layer and, hence, generally allow diffusion of adsorbates along more than one direction. Here, we report on the diffusion of individual 9,10-dithioanthracene (DTA) molecules on Cu(111). DTA adsorbs with the aromatic system lying flat on the substrate. In variable-temperature STM studies, we find that it diffuses exclusively in the direction in which it aromatic moiety happened to adsorb. We neither find rotation of the molecule in the surface plane nor diffusion perpendicular to the aromatic axis of the molecule. We investigated the dynamics of the one-dimensional diffusion of DTA and find an energy barrier of 130mev and an attempt frequency of 4 GHz. Density Functional Theory modeling of the diffusion potential shows, that DTA achieves unidirectional motion by sequential placement of its two substrate linker in a fashion that strikingly resembles bipedal locomotion.

3:00pm **SS1-ThA4 Bustling Bi/Cu(111): Phase Transitions and Atomic Structure***, **R. van Gastel**,* University of Twente, The Netherlands*; D. Kaminski, E. Vlieg,* Radboud University Nijmegen, The Netherlands*; B. Poelsema,* University of Twente, The Netherlands

We have combined surface X-ray diffraction (SXRD) and low-energy electron microscopy (LEEM) to investigate atomic structure and pattern formation in the Bi/Cu(111) system. Deposition of submonolayer amounts of Bi on Cu(111) leads to the formation of a two-phase system consisting of a surface alloy phase and an overlayer phase that forms patterns similar to those previously observed in the Pb/Cu(111) system.@footnote 1,2@ The patterns however exhibit several phase transitions that are unseen in Pb/Cu(111). Through SXRD measurements investigating the structure of the different surface phases,@footnote 3@ the origin of these transitions can be pinpointed to changes in the atomic structure of those phases. A rich variety of surface phases, covering the whole spectrum, from solid to liquid to lattice-gas-like and from ordered to disordered is observed. In LEEM movies, structural contrast between e.g. solid and liquid Bi overlayers lets us image the pattern dynamics and phase transitions directly. The pattern dynamics and the dramatic changes that occur during the transitions are analyzed to extract information and quantify the thermodynamic quantities that control the rich phase behavior in this system. @FootnoteText@ @footnote 1@ R. Plass, N.C. Bartelt and G.L. Kellogg, J. Phys. Cond. Mat. 14 (2002), 4227.@footnote 2@ R. van Gastel, R. Plass, N.C. Bartelt and G.L. Kellogg, Phys. Rev. Lett. 91 (2003), 055503.@footnote 3@ D. Kaminski, P. Poodt, E. Aret, N. Radenovic and E. Vlieg, Surf. Sci. 575 (2005), 233.

3:20pm **SS1-ThA5 Quantum Stabilization of Atomically Flat Films of Pb at 300 K***, **R. Miranda**,* Universidad Autónoma de Madrid, Spain **INVITED**

The 1D confinement of electrons within quantum wells produces a set of new states, the quantum well states (QWS), which may influence substantially the electronic energy and, thus, the total energy of the system. Pb grown on Cu(111) shows these effects in the form of "magic heights" for the 3D nanoislands that appear upon deposition at 300K.@footnote 1@ The "magic heights" are equivalent to the "magic numbers" reported for clusters, He droplets or nuclei. Deposition of Pb at 60 K, however, produces flat, metastable films that cover uniformly the Cu substrate. Their thicknesses can be determined by the characteristic energy of the QWS measured with Tunnelling Spectroscopy. The films grow layer by layer at low temperatures because of kinetic constraints, but upon heating, they decompose into the heights more stable. The dynamics of the thermal evolution of films of different thicknesses is explored by movies recorded with a Variable Temperature STM and compared to electronic energy calculations. We find that each Pb thickness becomes unstable at a different temperature (with films with QWS at the Fermi level (such as 9 ML-thick) being particularly unstable), while layers with thickness corresponding to "magic heights" are more stable. Some thicknesses are particularly stable, giving rise to atomically flat films of Pb over micron scales even at room temperature. @FootnoteText@@footnote 1@R. Otero, A.L. Vazquez de Parga and R. Miranda, Phys. Rev. B 55, 10791 (2002).

4:00pm **SS1-ThA7 Atom Transport in One-Dimensional Surface Diffusion***, **G. Antczak**, G. Ehrlich,* University of Illinois at Urbana-Champaign

We present an investigation of self-diffusion on the W(211) plane, done using atomic resolution field ion microscopy, which gives insight into the mechanism of migration of atoms in a one-dimensional system. We distinguish two temperature regions in diffusion over this surface. A low temperature region, where diffusion proceeds by the standard, well-known mechanism - jumps to nearest-neighbor sites, and a slightly higher temperature region, where double transitions start to play a significant role. The transition between these two regions is gradual. The existence of double jumps starts to be non-negligible at a temperature T = 310 K and the ratio of double to single transitions reaches 0.66 at a temperature T =

325 K. The importance of transitions occurring during the transient time is also examined. To get information about ratios of long jumps, the distributions of displacements consisting of 1200 observations for each temperature, is analyzed for regular measurement as well as for transient time measurements. In the lower temperature range, 300 measurements for each temperature are used to establish an Arrhenius plot for the diffusivity. For the first time it is shown that long transitions raise the prefactor for the diffusivity above the usual values. However, this increase is smaller than expected from a model of independent jumps. Activation energies and prefactors for double as well as single transitions are derived. A mechanism of long transitions on W(211) is proposed and compared to the mechanism for two-dimensional diffusion on W(110). Research supported by the Department of Energy under Grant No. DEFG02-91ER45439 to the Materials Research Lab.

4:20pm **SS1-ThA8 Diffusion and Ordering of CO Coadsorbed with H on Pd(111) Studied by Variable-Temperature STM***, T. Mitsui,* Lawrence Berkeley National Laboratory*; M.K. Rose, E. Fomin,* University of California, Berkeley*;* ***D.F. Ogletree****, M. Salmeron,* Lawrence Berkeley National Laboratory

CO adsorbs on Pd(111) in fcc hollow sites at low coverage. As coverage increases, ordered @sr@3x@sr@3 domains form with 1/3 of fcc sites occupied by CO. At higher coverage c(4x2) domains form with a density of 1/2, with CO adsorbed in either bridge sites, or in fcc and hcp hollow sites. Additional CO structures are formed at still higher coverage. H also adsorbs on Pd(111) in fcc sites, forming ordered @sr@3x@sr@3 domains with first 1/3 then 2/3 of fcc hollow sites occupied by H. At still higher coverage, H occupies all fcc sites forming 1x1 domains.@footnote 1@ When H was adsorbed on Pd(111) pre-covered with 0.12 to 0.33 ML of CO, the CO was compressed into c(4x2) domains, however higher-density CO domains were not observed even in a constant background pressure of 10@super -7@ Torr H@sub 2@. Co-adsorption of H has little effect on the diffusion of isolated CO molecules until the H coverage approaches 1/3 ML. At this point the CO diffusivity drops more than two orders of magnitude. CO diffusivity rises significantly as the H coverage passes 1/3 ML, then drops again as coverage approaches 2/3 ML. Very stable CO clusters were observed as H coverage approached 1 ML. Isolated CO molecules could be followed by STM up to ~ 110 K, while isolated CO diffusion on clean Pd(111) can be observed by STM as low as 45 K, and becomes to fast to follow by ~ 55 K. In small clusters CO molecules occupy both fcc and hcp sites, and diffusivity is a dramatic function of cluster size. 2 and 4 molecule clusters diffuse significantly faster than 1, 3 or 5 molecule clusters, and cluster diffusivity generally increases with size up to at least 7 CO molecules. The implications of these observations for inter-adsorbate interactions will be discussed. @FootnoteText@ @footnote 1@ M. K. Rose et al, Surface Science 2002, T. Mitsui et al, Surface Science 2003, T. Mitsui et al, Phys. Rev. Lett. 2005.

4:40pm **SS1-ThA9 Sintering of Au Clusters Supported on TiO@sub 2@(110): An In-Situ Scanning Tunneling Microscopic Study***,* ***F. Yang,*** Texas A&M University*; A. Kolmakov,* University of California at Santa Barbara*; A.K. Santra,* Halliburton Company*; D.W. Goodman,* Texas A&M University

Sintering, i.e. an increase in the average size of nanoclusters, is a frequently encountered problem in nanotechnology and a principle cause of deactivation in nanocatalysts. For example, Au supported on high-surface-area titania is a highly efficient catalyst for selective oxidation and hydrogenation reactions; however, commercial development is seriously hampered because Au nanoclusters sinter rapidly. The mechanisms of sintering are not well understood and depend, to a large extent, on understanding elementary surface diffusion processes. Scanning tunneling microscopy (STM) is capable of atomic-level measurements over a variety of conditions. In-situ STM allows the morphological changes of specific nanoclusters to be monitored over a variety of reaction conditions from ultrahigh vacuum to realistic reactant pressures. Using in-situ STM, the growth kinetics of Au on TiO@sub 2@(110) have been measured directly, allowing sintering mechanisms to be proposed for supported Au model catalysts under realistic reaction conditions. The STM results also show that substrate hydroxylation blocks the preferential growth of Au clusters and alters their growth kinetics on a TiO@sub 2@(110) surface. Furthermore, the sintering kinetics of Au clusters during the CO oxidation reaction have been studied for Au clusters supported on TiO@sub 2@(110) and on hydroxylated TiO@sub 2@(110).

Surface Science
Room 203 - Session SS2-ThA
Gas-Surface Reaction Dynamics

Moderator: K.W. Kolasinski, University of Virginia

2:00pm **SS2-ThA1 Why is Formate Synthesis Insensitive to Copper Surface Structures?***,* ***J. Nakamura,*** University of Tsukuba, Japan*; Y. Morikawa,* Osaka University, Japan*; G. Wang,* Nankai University, China

Unique structure sensitivity has been experimentally observed for the formate synthesis from CO@sub2@ and H@sub2@ (CO@sub2@ + 1/2 H@sub2@ ---> HCOOa) on copper surfaces and the reverse reaction of formate decomposition. That is, the reaction rate of formate synthesis and the activation energy are very similar among Cu(110), Cu(100), and Cu(111), meaning a structure insensitive reaction. On the other hand, the reverse reaction of formate decomposition on copper was a structure sensitive reaction with different activation energies. Also, an Eley-Rideal (E-R) type reaction mechanism has been suggested for the formate synthesis, in which CO@sub2@ molecule directly reacts with adsorbed hydrogen without passing through adsorption of CO@sub2@. Here, we report the results of ab initio density functional theory (DFT) calculation for the formate synthesis. The DFT-GGA calculation has reproduced adsorption energies and adsorption structure of bidentate formate experimentally measured on Cu(111), Cu(100), and Cu(110), which further reproduces the structure insensitive and structure sensitive features for formate synthesis and formate decomposition, respectively. The structure insensitivity is due to the presence of monodentate formate with similar adsorption energies on Cu(111), Cu(100), and Cu(110), giving a similar energetic pathway from CO@sub2,g@ + 1/2 H@sub2,g@ to monodentate formate. The structure sensitive feature for the decomposition of bidentate formate is due to a significant difference in the adsorption energy of bidentate formate depending on the Cu surface structure. The structure insensitivity is due to the E-R type reaction mechanism without passing through adsorption of CO@sub2@, which enables a similar reaction pathway with similar local structures as revealed in the snapshot for the structural change of intermediates.

2:20pm **SS2-ThA2 Experimental and Computational Probes of Transition States on Surfaces***,* ***A.J. Gellman****, D.S. Sholl, P.P. Ye, X. Li,* Carnegie Mellon University

Transition states determine the rates of surface catalyzed reactions, however, direct characterization of surface transition states is challenging. Experimental measurements of substituent effects on reaction barriers have been combined with Density Functional Theory to probe the transition states to the @beta@-hydride elimination in ethoxy groups on Cu(111) and the hydrogenation of alkyl groups on Pt(111). Our results allow us to test the recently advanced proposition that surface reactions with reactant-like (product-like) transition states are relatively sensitive (insensitive) to the nature of the catalyst surface. The barrier to @beta@-hydride elimination in fluorine substituted ethoxy groups increases significantly as a result of fluorine substitution. This is ascribed to a transition state in which the @beta@-carbon atom is cationic with respect to the initial state ethoxy group. Comparison of the experimental values of @Delta@E@sub act@ and the predictions of DFT shows impressive agreement and verifies the predictions based on previous experimental measurements. Substituent effects have been used to probe the characteristics of the transition states to hydrogenation of alkyl groups on the Pt(111) surface and the transition state to @beta@-hydride elimination in alkyl groups on the Pt(111) surface. Co-adsorption of hydrogen with alkyl groups and subsequent heating of the surface results in hydrogenation of the alkyl groups to alkanes which desorb into the gas phase. The influence of the substituents on the activation barriers to hydrogenation has been correlated with the field and polarizibility substituent constants of the alkyl groups in the form of a linear free energy relationship. This indicates that the @alpha@-carbon in the transition state is cationic with respect to the initial state alkyl group and that the reactant has greater charge density on the @alpha@-carbon than the transition state.

2:40pm **SS2-ThA3 Molecular Beam Studies of Rare Gas and HCl Collisions with Functionalized Self-Assembled Monolayers***, B.S. Day, L.R. Fiegland,* ***J.R. Morris,*** Virginia Tech **INVITED**

The research objectives of this work are aimed at elucidating the atomic-scale mechanisms of interfacial bonding, diffusion, and reactions that govern gas-surface interactions on organic surfaces. This challenge is particularly formidable for functionalized organic surfaces where the complicated nature of the interface can result in a broad range of reaction pathways. The approach used in these studies for exploring gas-surface reaction mechanisms combines molecular beam scattering techniques with functionalized self-assembled monolayers. Together with surface analysis instrumentation, these techniques are designed to reveal insight into many aspects of the gas-surface interaction and help develop an atomic-level description of the transformation of reactants into products. This presentation will focus on recent investigations into the dynamics of rare gas and HCl collisions with self-assembled monolayers. Atomic beams of high-energy rare gases are employed to explore the initial gas-surface collision in the absence of reactivity. These studies reveal how the atomic-scale nature of organic surfaces determine the extent of interfacial energy transfer and the path to thermal accommodation. The atom scattering studies are used to help interpret the dynamics of reactive gas-surface collisions, such as HCl impinging on a hydroxylated surface. In this work, HCl is directed at OH-terminated self-assembled monolayers to learn about how gas-surface hydrogen-bonding forces influence the dynamics of the collision. Measurements of the HCl energy transfer, residence time, and proton exchange probability have provided new insight into the interactions of HCl with well-characterized hydroxylated surfaces.

3:20pm **SS2-ThA5 Gas-Surface Reaction Dynamics of NO on Iron Phthalocyanine Thin Films***, **S.R. Bishop**, N.L. Tran, G.C. Poon, A.C. Kummel,* University of California, San Diego

Metallophthalocyanines (MPc) have been proposed for use in chemically sensitive field effect transistor (chem-FET) detectors for the measurement of ambient analytes such as NO@sub x@, NH@sub 3@, and O@sub 3@. However, the adsorption energies and mechanisms of the reaction between these gases and MPc thin films have not been studied. We have investigated the reaction dynamics between NO and monolayer Iron Phthalocyanine (FePc) grown on clean Au(111) surface. The sticking probabilities of 0.11 eV monoenergetic molecular beam of NO were measured on both clean Au(111) and ordered 6x6 monolayer-FePc deposited on clean Au(111) as a function of surface temperature. NO sticking on the Au(111) surface occurs through a precursor-mediated physisorption pathway. In comparison, NO sticking on the FePc film occurs via multiple pathways: direct chemisorption to the metal center and precursor-mediated physisorption. Although the metal center of the molecule accounts for only ~3% of the surface, the direct chemisorption pathway has a sticking probability of ~20%. This suggests that the NO molecules are steered to the reactive metal centers by other portions of the FePc molecule. By using a high translational energy molecular beam, the direct chemisorption pathway will be selectively probed.

3:40pm **SS2-ThA6 Extracting the Vibrational Ground State Reactivity of Methane on Ni(111) from Ensemble Averaged Experiments***, **D.R. Killelea**, V. Campbell, A.L. Utz,* Tufts University

Beam-surface studies have uncovered key details of the dynamics of methane dissociation on transition metal surfaces. When the measured reactivity is averaged over the population distribution of vibrational states in the beam, the data may obscure the role of individual vibrational states in promoting reaction. Here, we measure the reactivity of CH@sub 4@ beams impinging on a Ni(111) surface. We vary the vibrational energy of the beams by changing the beam source temperature. We model the nozzle temperature effect for these data, and extrapolate to find the reactivity of CH@sub 4@ in its vibrational ground state (v=0). Our model predicts that at the low translational energies typical of thermal samples, vibrationally excited molecules account for the majority of observed reactivity.

4:00pm **SS2-ThA7 Variable (T@sub g@, T@sub s@) Measurements of Alkane Dissociative Sticking Coefficients***, **K.M. DeWitt**, L. Valadez, K.W. Kolasinski, I. Harrison,* University of Virginia

A novel technique for measuring nonequilibrium dissociative sticking coefficients, S(T@sub g@, T@sub s@), with well-defined gas temperature, T@sub g@, and surface temperature, T@sub s@, is described, along with its application to activated dissociative chemisorption of CH@sub 4@ and C@sub 2@H@sub 6@ on Pt(111). Microcanonical unimolecular rate theory (MURT) is employed to analyze the sticking coefficients and to extract transition state characteristics. The MURT allows the S(T@sub g@, T@sub s@) sticking to be directly compared to other molecular beam and thermal equilibrium sticking measurements. Interestingly, measured S(T@sub g@ = 300 K, T@sub s@) for CH@sub 4@ on Pt(111) are several times larger than recent thermal equilibrium measurements, S(T@sub g@ = T@sub s@), on supported Pt nanocrystallite catalysts [J. M. Wei, E. Iglesia, J. Phys. Chem. B 108, 4094 (2004)]. This is a surprising result that runs contrary to the popular notion that dissociative chemisorption should be enhanced at the coordinatively less saturated defect sites that should be more prevalent on the ~2 nm diameter Pt nanocatalysts than on a flat Pt(111) surface.

4:20pm **SS2-ThA8 First Principles Resonance Energies and Widths of Ions near Surfaces: N-Body Dynamical Predictions of Charge-Transfer Probabilities for Scattered Ions***, **K. Niedfeldt**, E.A. Carter,* Princeton University*; P. Nordlander,* Rice Univeristy

By combining periodic density-functional theory calculations of adsorbate resonance widths and shifts with a many-body dynamical charge-transfer theory, we quantitatively assess charge-transfer rates for ions scattering off surfaces. This method goes beyond previous approaches, which have been limited to modeling metal surfaces with either jellium potentials or finite clusters. We consider Li+ scattering off Si(001), Mg(0001), Cu(001), and Al(001). When compared to experimental neutralization fractions for Li ion scattering off of Al(001), our method yields trends in neutralization as a function of scattering angle in better agreement than those derived from jellium models. Our results comparing Mg and Cu show that scattering off of Mg and Cu yield distinctly different charge-transfer probabilities. By contrast, jellium predicts identical scattering properties due to identical theoretical free-electron gas values. As expected, for Li ions scattering off Si(001), the Li 2s orbital interacts most strongly with the Si dimer dangling bonds. The charge-transfer rates for Li ions scattering off Si(001) exhibits extreme variations with lateral position, in contrast again to the jellium picture. Taken together, these results clearly indicate that more realistic ion-surface interaction models (such as provided here) are necessary to obtain even qualitatively correct trends in charge-transfer for many ion-surface interactions.

4:40pm **SS2-ThA9 Formation of Multiply Charged Ions by Direct Recoil***, **X. Chen**, Z. Sroubek, J.A. Yarmoff,* University of California, Riverside

Low energy ions that impact a solid surface can remove material by sputtering, which produces low kinetic energy particles through a collision cascade, or direct recoil (DR), which involves the emission of a relatively high-energy particle following a hard collision between the incident ion and a surface atom. An inner-shell promotion that places one of the atoms into an excited state is a possible consequence of the hard collision. In these experiments, we find a unique process in which the DR particle is emitted with two holes, i.e., as a doubly charged ion. Si@super +@ ions were incident on atomically clean Al(100). The absolute ionization probability of scattered Si and recoiled Al were measured with time-of-flight, while detailed spectra of the ion yield were collected with an electrostatic analyzer. All of the scattered Si was neutralized, as expected due to its large ionization potential. Spectra collected of the DR Al show, however, a combination of Al@super 1+@, Al@super 2+@ and Al@super 3+@ ions. The multiply charged ions are attributed to a charge promotion of the Al 2p during the hard collision. The Al 2p level is promoted above the Fermi energy by interaction with the Si 2p level that lies just below, such that both electrons are transferred to the solid forming Al ions with two holes. Subsequently, some of the Al@super 2+@ may decay to Al@super 3+@ via autoionization, or pick up an electron to form Al@super 1+@. This mechanism is verified by the observation of an energy threshold for the process, and by spectra of the electrons emitted as the excited states decay. This process of producing multiply charged DR ions is highly effective because of the small separation between the Al and Si 2p levels. Thus, it is expected that similar behavior would occur for other closely matched systems that will be investigated, such as P ions incident on solid Si.

Thin Films
Room 306 - Session TF+EM-ThA
Transparent Conducting Oxides

Moderator: S. Gupta, The University of Alabama

2:00pm **TF+EM-ThA1 Transparent Conducting Oxides***, **J.C.C. Fan**,* Kopin Corporation **INVITED**

Transparent Conducting Oxides (TCO) have enormous practical applications in energy-conserving heat mirrors, in solar-energy collectors, solar photovolactic and in electronic devices such as liquid crystal displays and light-emitting diodes. These oxides which are transparent in the visible spectrum are yet electrically conducting have been around for many decades. The most popular ones are In2O3-doped with Sn, and SnO2-doped with Sb. These two classes of TCOs have been extensively researched for many years and their results and applications will be reviewed. In addition, there are newer TCOs in the fields, such as MoO3, ZnO, and others. Their status and potential will also be discussed.

3:00pm **TF+EM-ThA4 Study on Initial Growth Process of Transparent Conductive Oxide Films Deposited by dc Magnetron Sputtering*, Y. Sato,*** *M. Taketomo, A. Miyamura, Y. Shigesato,* Aoyama Gakuin University, Japan

It has been noticed that surface defects such as spike or pinhole of transparent conductive oxide (TCO) films should cause the degradation on the performance of organic organic light emitting diode (OLED) displays as appearances of dark-spots. In order to improve their performances, the film surface morphology has been required to be extremely flat. Such surface morphology should be highly related to the initial growth processes of the thin film electrodes. In this study, we investigated the early stages of film growth of representative TCO films such as ITO (Tin doped Indium oxide), IZO (Indium Zinc oxide) and GZO (Gallium doped Zinc oxide) deposited by sputtering. These films with thickness of 5-200 nm were deposited on unheated non-alkali glass substrates by dc magnetron sputtering under a various total gas pressures of Ar/O@sub 2@ mixture gases. The surface morphology of the films was analyzed quantitatively by atomic force microscope (AFM). The average roughness (Ra) of ITO and GZO films with the nominal thickness of 5 nm, deposited under 1.0 Pa, reached maximum of 0.4 and 0.8 nm, respectively. Ra of the both films decreased and remained constant around 0.2 and 0.4 nm, respectively, with the farther increase in thickness larger than 25 nm. These trends implied that three dimensional (Volmer-Weber) growth occurs for the polycrystalline ITO or GZO films, i.e. after an initial nucleation, an island structure grew and coalesced with each other with increasing film thickness. This expectation is consistent with the electrical properties of these films. On the other hand, Ra for the amorphous IZO film remained constant with the increasing nominal thickness from 5 to 200 nm. It must be considered that a nucleation density of IZO film should be much higher than those of ITO or GZO films. This work was partially supported by a Grant-in-Aid for 21st COE Program from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government.

3:20pm **TF+EM-ThA5 Transparent Conducting Oxide Deposition using Closed Field Reactive Magnetron Sputtering*, J.M. Walls,*** *D.R. Gibson, I. Brinkley, E.M. Waddell,* Applied Multilayers Ltd, UK

Magnetron Sputtering has many advantages for the deposition of optical coating materials. The sputtering process is "cold", making it suitable for use on the widest range of substrates including damage sensitive polymers. This paper will describe a "Closed Field" reactive sputtering process that allows high quality, transparent conducting oxide (TCO) thin films to be deposited at high rates. In contrast to previous reactive dc sputtering strategies the Closed Field process does not require a separate energetic ion or plasma source. The Closed Field automatically creates a magnetic confinement that extends electron mean free paths and leads to high ion current densities (>1mA.cm@super -2@). The combination of high current densities with ion energies in the range 15eV to 30eV creates optimum thin film growth conditions. As a result the films are dense, spectrally stable and exceptionally smooth (rms roughness

3:40pm **TF+EM-ThA6 Effect of Dendrimer Underlayers on Sputtered Indium-Tin Oxide Thin Film Microstructure, Morphology, Optical and Electrical Properties*, R. Thunuguntla,*** *S. Gupta, S. Street,* The University of Alabama*; D. Loy,* The Army/ASUFlexible Display Center

Minimization of surface roughness is extremely important for sputtered indium-tin oxide (ITO) films used for organic light-emitting diode (OLED) applications. One of the techniques used to achieve smooth ITO films is the optimization of process parameters together with injection of cesium vapor into the plasma -- the recently-introduced negative sputter ion beam or NSIB process.@footnote 1@ We have investigated an alternative simpler approach -- the application of dendrimer monolayers by dip- or spin-coating techniques prior to ITO sputter deposition at ambient temperatures. The ITO films have been characterized by X-ray diffraction (XRD) and atomic force microscopy (AFM), and the film microstructure and morphology have been correlated with the optical and electronic properties such as transmission, resistivity, mobility and carrier concentration. The presence of the dendrimer underlayer appears to mediate the film roughness by grain size reduction and improved adhesion. The greatest effect is seen in films sputtered at low powers. This is expected, since a high level of ion bombardment is expected to damage or destroy the dendrimer underlayer. The observed improvement is most encouraging for flexible display applications, where good film properties and low surface roughness are required at low deposition temperatures. @FootnoteText@ @footnote 1@ M. H. Sohn et al., J. Vac. Sci. Technol. A21(4), 1347 (2003).

4:00pm **TF+EM-ThA7 Ferromagnetic Behavior in Indium Oxide Based Transparent Semiconductors*, J. Moodera,*** Massachusetts Institute of Technology **INVITED**

Ferromagnetic semiconductors are expected to provide smooth transition for spin injection and transport needed for spin based technology leading to multifunctional devices of the future. Although the field of dilute magnetic semiconductors has been explored for a long time, in recent years there is increased activity due to the significant increase in the ferromagnetic ordering temperature (T@sub c@) of Ga@sub 1-x@Mn@sub x@As system and in various doped oxide systems, despite the existing skepticism in the latter area. We have observed ferromagnetism well above room temperature in Mn doped indium-tin oxide (ITO), Cr doped indium oxide (IO) as well as Mn doped zinc oxide films by reactive evaporation as well as sputtering. Films grown on sapphire (0001) and on silicon show excellent magnetic behavior with a moment ranging from 1 to 5µ@sub B@ for low concentrations of the dopant. Mn doped ITO and Cr doped IO are highly transparent as well as conducting. The electrical conduction is n-type with a carrier concentration in the range of 10@super 18@ to 10@super 20@ cm@super -3@. The charge carriers are seen to be spin polarized shown by the presence of anomalous Hall effect, revealing the magnetic interaction between itinerant electrons and localized Mn or Cr spins. What is interesting in these compounds is that the charge carriers can be independently varied independent of the dopant by the oxygen or the tin concentration in this transparent semiconductor for its easy integration into magneto-optoelectronic devices. In this talk the status of the field will be reviewed and compared with our work. Work carried out in collaboration with John Philip and Nikoleta Theodoropoulou. Supported by the CMI funds at MIT and NSF funds.

Applied Surface Science
Room 206 - Session AS-FrM

Practical Methods and Applications for Surface Analysis

Moderator: M.C. Burrell, GE Global Research Center

8:20am **AS-FrM1 ToF-SIMS Measurements of a Fluorocarbon-based Self-Assembled Monolayer on Si***, **J.A. Ohlhausen**, K.R. Zavadil,* Sandia National Laboratories

Low surface energy coatings and films are needed to minimize stiction, high friction and wear of the oxide-terminated silicon-based MicroElectroMechanical Systems (MEMS) to ensure reliable device function. One common approach is to deposit self-assembled monolayer (SAM) films containing reactive silane headgroups and low energy pendant chains to cover the complex structures used in MEMS devices. The composition of these films is difficult to characterize and quantify (a property or quality is quantified composition, an aspect of structure, etc.). Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is an ideal tool for characterizing these types of films, however interpretation of the spectral data generated is complex and challenging. We are using the combination of X-ray Photoelectron Spectrometry (XPS) and ToF-SIMS to detect and quantify several candidate fluorocarbon-based SAMS on Si coupons and on MEMS devices. Unexpected fragmentation caused by the interaction of the primary ion beam with the fluorocarbon chain in contact with the Si surface creates ions whose presence are not intuitive. We can account for these ion fragments and use them to aid in quantifying the film composition. Our methods include the use of coverage-dependent fragmentation signatures along with the application of multivariate statistical techniques to establish the co-variance in these signatures. The fragmentation seen in this system along with the quantification method we used will be presented. @FootnoteText@ Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energys National Nuclear Security Administration under contract DE-AC04-94AL85000.

8:40am **AS-FrM2 XPS-imaging; Investigation of the Potentials of a Recent Algorithm Applied to a Patterned Polymer***, S. Hajati,* University of Southern Denmark*; S. Tougaard,* University of Southern Denmark, Denmark*; **S.J. Coultas**, C.J. Blomfield, C. Moffitt,* Kratos Analytical Ltd, UK

We have investigated the practical potentials of a recent algorithm for automatic data processing of XPS spectra.@footnote 1@ For each XPS peak, this algorithm determines the total amount of the corresponding atoms within the outermost ~ 3 inelastic electron mean free paths and it also gives an estimate of their depth distribution. The validity of the algorithm was recently tested@footnote 2@ by analysis of conventional (low lateral resolution) XPS measurements from layered samples. It was found to be very accurate and robust and much superior to usual analysis which relies on peak areas. In this paper we have studied spectra acquired at high lateral resolution (~2µm) of a patterned hydrophilic plasma polymer deposited on to a PTFE substrate. The spectra are reconstructed from a series of parallel photoelectron images recorded using a pulse counting delay line detector. For each pixel, we have used the C1s, F1s and O1s peaks to determine the amount of atoms as well as their approximate depth distribution for each element. The method is less accurate than the traditional QUASES-peak shape analysis method. However the latter requires operator interaction and is not practical for XPS imaging where thousands of spectra must be analyzed. @FootnoteText@ @footnote 1@ S. Tougaard, J. Vac Sci. Technol. A21, 1081 (2003)@footnote 2@ S. Tougaard, J. Vac. Sci. Technol. 2005, In press .

9:00am **AS-FrM3 Surface Analysis in Modern Industry - More, Faster, Cheaper, Better?***, **I.W. Fletcher**, S.F. Davies,* ICI plc, UK **INVITED**

The driving aim of most industrial activity is to make money by producing and selling products that people need or want and many processes and products involve surfaces or surface chemistry issues where surface analysis can deliver significant benefits. Research and development along with process and product problem solving are the obvious areas, although SHE, patent protection and various legal applications are also important. There is pressure on most businesses to increase profitability and to reduce costs, with analysis all too often being seen as pure cost. The 'do more, faster, cheaper' requirement may seem to conflict with the unwritten requirement to 'do it right'. Industrial analytical problems can and do provide significant challenges, often pushing analysts, instrumentation and techniques to the limits of what is possible. Fortunately modern equipment is now more reliable, often automated and is also capable of producing better quality data with much higher signal to noise levels and with better resolution than before. These help with the speed and accuracy of analysis and also open up new areas of information that were previously inaccessible. For example, images of the various species on the surface can be critical to a complete understanding of the situation and to many product developments. Using static SIMS with polyatomic and cluster ion beams, it is now routinely possible to generate images from truly molecular species rather than from elemental or small fragment ion species. This presentation will outline several practical examples using SSIMS and XPS applied to 'industrial' samples including man-made fibres, hair, foodstuffs and catalysts.

9:40am **AS-FrM5 Comparison of Methods for the Quantification and 3D Characterization of Polymer Blends using XPS and CLSM***, **J.L. Fenton**, K. Artyushkova, J.E. Fulghum,* University of New Mexico

The complete characterization of a heterogeneous polymer blend often requires multiple analytical techniques; each of the techniques providing limited data compared to the total information required. The most effective approach to multitechnique analysis utilizes data acquired from the same area on the same sample. However, there are still a number of issues to be resolved if quantitative multitechnique fusion is to be utilized. This study evaluates methods for quantifying phases observed in confocal laser scanning microscopy (CLSM) images. CLSM images can have a lateral resolution comparable to or better than XPS images, provide information on fluorescent polymer phase distribution, and 3D volumes can be created by changing the focal plane. In this talk we evaluate the use of CLSM images to quantitatively investigate phase distributions in polymer blends as a function of depth. CLSM image quantification methods including using image intensity calibration beads with vertical polymer blend distribution standards, analytical treatment of CLSM optics and fluorescence properties, and correlation with XPS images are compared. The quantitative concentration data is then used to create a 3D volume containing chemical and elemental concentration information. This work has been partially supported by NSF CHE-0350666, the UNM NSF IGERT CORE DGE-00114319 and UNM.

10:00am **AS-FrM6 X-ray Photoelectron Spectroscopic Study of an Oxygen-doped Zinc Sulfide Surface Using Sample Biasing***, **Y.-Q. Wang**, P.M.A. Sherwood,* Oklahoma State University

X-ray photoelectron spectroscopy (XPS) was used to study the surface chemistry of zinc sulfide (ZnS) exposed to a number of oxidation treatments at various conditions to understand the effect of oxygen on surfaces of II-VI compounds. These compounds are widely used as luminescence and window materials, where the mechanism of the effect of oxygen interaction and its effect on the properties and applications of these materials, has not been clearly understood. The oxygen was introduced onto the ZnS surface by heat-treating the sample in a furnace with water vapor and by synthesis of ZnS. The core XPS studies were conducted with and without the application of a sample bias potential, and showed that oxygen interaction caused a considerable change in the surface chemistry of ZnS. The application of a positive bias led to a shift in the core XPS peaks expected for a conductive material, but the negative bias gave rise to unusual behavior. In the case of ZnO the core XPS peaks behaved in the way expected of a conducting material under positive or negative bias. The ZnS samples exhibited a peak shift that was closely related to the oxygen content in the surface region. Furthermore, the sample synthesized in aqueous solution resulted in peak splitting under a negative bias. The surface chemistry monitored by XPS, and the interpretation of the biasing shifts allows for a better understanding of the change of luminescence phenomena in ZnS materials involving oxygen.

10:20am **AS-FrM7 Thin Oxide Free Phosphate Films of Novel Composition formed on the Surface of Vanadium Metal and Characterized by X-Ray Photoelectron Spectroscopy***, D.J. Asunskis, **P.M.A. Sherwood**,* Oklahoma State University

This paper reports the preparation of thin (less than 100 Angstroms) oxide-free phosphate films of various compositions on vanadium metal. These films are interesting because of their potential for corrosion inhibition, adhesion promotion and biocompatibility. Valence band and core-level X-ray photoelectron spectroscopy (XPS) were used to characterize the films. The valence band spectra obtained were compared with spectra generated from band structure calculations for various vanadium phosphates and from previously reported spectra of vanadium phosphates. Novel vanadium phosphate coatings were created by the reaction of vanadium metal and different phosphorus-oxygen containing acids, H@sub 3@PO@sub 4@, H@sub 3@PO@sub 3@, H@sub 3@PO@sub 2@ and H@sub 4@P@sub 2@O@sub 7@. The paper focuses upon the valence band region which shows significant differences between the three vanadium phosphate films formed as well as clear differences between the three phosphates and vanadium oxides. The valence band spectra are effectively interpreted by band structure calculations. @FootnoteText@ The work was supported by the National Science Foundation under Grant No. CHE-0137502.

10:40am **AS-FrM8 Surface Characterization of Metal Exchanged Mesoporous Materials*, S.G. MacKay,*** University of Maine, US*; K.D. Bishop, B.K. Schaefer, J.D. Anderson, J.C. Bolton, H.H. Patterson,* University of Maine

We are investigating the role of transition metal clusters in heterogeneous photocatalysts used for the remediation of a variety of toxic organic compounds. These catalysts have already been successfully employed in remediating organophosphorous and carbamate compounds,@footnote 1@ and they have also been shown to be robust in the presence of dissolved organic carbon.@footnote 2@ The design of these catalysts involves incorporating metal ions into mesoporous materials via ion exchange. Manipulation of the support material geometry and the metal ion composition provides control over the catalyst selectivity and reactivity. Currently we are expanding our application areas to include biological target molecules and organisms. For these studies we have covalently attached zeolite and MCM photocatalysts onto a polymer surface using a methacryl silane. XPS was used to study both the catalyst/polymer attachment chemistry as well as the surface oxidation states of the photocatalytic metal sites. Catalysts studied include faujasite zeolites at different Si/Al ratios exchanged with Ag as well as with mixed metals (Ag/Cu). The correlation of these results with earlier published work using photoluminescence will be shown along with data from both TOF-SIMS and high resolution TEM analyses of these same materials. @FootnoteText@ @footnote 1@J. Phys. Chem. B. 2001, 105, 7508-7516.@footnote 2@Envir. Sci. Technol. 2003, 37, 2280.

11:20am **AS-FrM10 Improving High Resolution AFM Images - When are Sharp Tips Worthwhile?*, C.F.H. Gondran,*** ATDF Inc., a subsidiary of SEMATECH*; D.K. Michelson,* ISMI, a subsidiary of SEMATECH

Recently, AFM probes with sharper tips (1-2 nm radii of curvature) have become commercially available. This provides broad access to an opportunity to improve high-resolution images. Under the right circumstances, these improvements are very dramatic.@footnote 1@ However, in other instances, sharp tips offer limited benefits and the additional cost may not be justified. This study is designed to improve our understanding of the benefits of using sharp tips and to help determine when these benefits can be realized. Two-dimensional geometric models@footnote 2@ are used to evaluate the effect of tip shape on AFM images, roughness values, and power spectral density curves obtained for a variety of sample types. The effects of tip size are studied as a function of the sample's surface roughness, average feature size, average feature spacing, and surface feature shape. The results, particularly for roughness values, are not always intuitive. The simulated data are correlated to sample data obtained on films commonly used in research and development for semiconductor manufacturing: epitaxial Si, high-k, low-k, and barrier layer materials. These correlations are used to assess the value of sharp tips for the semiconductor industry. @FootnoteText@ @footnote 1@ D. Klinov, S. Magonov "True molecular Resolution in Tapping-Mode Atomic Force Microscopy with High-Resolution Probes," Applied Phys. Letts., 84(14) 2004, p. 2697.@footnote 2@ C. F. H. Gondran, D. K. Michelson "Sampling and Reference Considerations for Very High Resolution AFM Analysis," in Proc. 30th International Symposium for Testing and Failure Analysis, ASM International, Ohio, 2004 p. 357.

11:40am **AS-FrM11 Microscopy Study of Composites Based on Propylene-Ethylene Copolymers*, L.L. Ionescu-Vasii,*** *P. Wood-Adams,* Concordia University, Canada*; E. Duschene,* Ecole Polytechnique de Montréal, Canada

MMany recent developments in polymer materials science have been triggered by the development of improved synthesis methods. As a consequence, a wide variety of polymers with unusual properties can be designed and synthesized. Recently, The Dow Chemical Company developed a new catalyst which allows copolymerization of propylene with various alpha-olefin comonomers over a broad range of compositions in isotactic fashion and with high molecular weight (SWOGGER K et al, 2003). Our interest focuses on a new family of propylene-ethylene copolymers produced by Dow Company, which has an exceptional ability to accept very high loadings (80% wt and higher) of fillers or/and additives, while maintaining good processability. The new propylene-ethylene (P/E) copolymers used in our study exhibit high molecular weights, low densities, relatively narrow molecular weight distributions and unique micro-molecular structures. The ethylene content of these copolymers ranges from 9 to 15 wt %. We report here the first results of our microscopy study of twelve composites (with 20, 40, 60 and 80 wt% calcium carbonate filler) based on three new propylene-ethylene copolymers. Different microscopy techniques (SEM, TEM, AFM) and different samples' preparation techniques (cryogenic microtomy, FIB, annealing) were used in order to obtain a thorough understanding of the microstructure of the composites studied and to evaluate the interaction between the filler particles and the polymer matrices. @FootnoteText@ @footnote 1@ SWOGGER K. W., POON B., ANSEMS P., CHUM S., HILTNER A. AND BAER E. (2003), Material classification and applications of new propylene-ethylene copolymers. SPE ANTEC Tec. Papers, 1768.

Biomaterial Interfaces
Room 311 - Session BI+SS-FrM

Biomaterials Surface Characterization

Moderator: S.L. McArthur, University of Sheffield, UK

8:20am **BI+SS-FrM1 Charge Injection Barriers and Gap States at the L-Cysteine/Au Interface*, M.M. Beerbom,*** *R. Gargagliano, R. Schlaf,* University of South Florida

Protein/inorganic materials interfaces are interesting for many bio-engineering applications such as bio-sensors or molecular electronic devices. L-cysteine is particularly interesting since it can form self-assembled monolayers on gold due to its thiol-group. In our experiments we investigated the L-cysteine/Au interface using x-ray and ultraviolet photoelectron spectroscopy (XPS, UPS) in combination with a multi-step deposition procedure. PE-spectra obtained after each deposition step yielded a data set allowing the determination of charge injection barriers at the interface, as well as the characterization of the chemical interaction. The L-cysteine deposition was carried out in a glove box directly attached to the PES system enabling contamination-free measurements. Our results indicate the formation of an interface state within the HOMO-LUMO gap due to the thiol-Au interaction.@footnote 1@ This is supported by control experiments on L-cysteine/graphite interfaces, which did not show the formation of this gap state. @FootnoteText@ @footnote 1@M.M. Beerbom, R. Gargagliano and R. Schlaf: "Determination of the Electronic Structure of Self-Assembled L-cysteine/Au Interfaces Using Photoemission Spectroscopy", Langmuir Articles ASAP), (2005).

8:40am **BI+SS-FrM2 Injection into Vacuum and Alignment of Biological Molecules for Electron Diffraction*, D. Starodub,*** *R.B. Doak, J.C.H. Spence, U. Weierstall, K. Schmidt, G. Hembree,* Arizona State University

Resolving the protein secondary structure (folding),critical for its functionality, is a demanding task, especially for the proteins, which cannot be easily crystallized. Recently it was proposed to collect diffraction patterns dynamically from an array of biological molecules embedded in submicron water droplets, consecutively traversing the intersection of a focused 50 keV electron beam and a polarized 100 W laser beam.@footnote 1@ The latter aligns the molecules due to field interaction with a dipole moment induced in the molecule with anisotropic polarizability tensor.@footnote2@ We show experimental results on generation of monodispersed microdroplets via growth of Rayleigh instability, their injection into high vacuum, evaporation and cooling. The limitations on the droplet size and temperature for a given jet source configuration are obtained. Rotational relaxation of the spherical (small protein) and rodlike (tobacco mosaic virus) biomolecules to thermal fluctuations about the equilibrium orientation is considered in viscous and free molecular flow regimes, and optimal conditions for alignment, sufficient to obtain sub-nanometer resolution in diffraction, are derived. We also consider adiabatic effects of different spatial profiles of laser beam intensity and droplet velocity on final oscillation states of a biomolecule. Supported by NSF funding SGER DBI-0429814. @FootnoteText@ @footnote1@J.C.H. Spence and R.B. Doak, Phys. Rev. Lett. 92, 198102(2004). @footnote2@J.C.H. Spence, K. Schmidt, J. Wu, G. Hembree, U. Weierstall, R.B. Doak, P. Fromme. Acta Cryst. A61, 237(2005).

9:00am **BI+SS-FrM3 Chemical Interaction Analysis of Adhesive Biomaterial-Hard Tissue Interfaces*, Y. Nakayama,*** Toray Research Center, Inc., Japan*; Y. Yoshida, K. Suzuki,* Okayama University Graduate School of Medicine, Dentistry and Pharmaceutical Sciences, Japan*; B. Van Meerbeek,* Catholic University of Leuven, Belgium

Adhesion to human hard tissue plays an important role in both dental and orthopedic therapies. Synthesized adhesive biomaterials made of polymer, as well as of functional monomer, have been developed. Among such adhesive biomaterials, those capable of forming chemical bond with hard tissue such as dentin, enamel or hydroxyapatite (HAp) are more appreciated for achieving more durable adhesion. Evidence of chemical bonding at biomaterial-hard tissue interfaces was recently reported for interfaces between polyalkenoic acid and enamel or HAp with the use of high resolution X-ray Photoelectron Spectroscopy (XPS).@footnote 1@ Preparation of ultrathin biomaterial molecular layer on enamel or HAp substrate enabled high resolution XPS spectrum to distinguish carboxylic carbons with chemical bond to HAp from those without chemical bond at the interface. Chemical interaction of carboxylic acids with HAp was analyzed and adhesion-decalcification concept (AD concept) was proposed.@footnote 2@ According to the AD concept, the less soluble the calcium salt of the acidic molecule, the more intense and stable the molecular adhesion to a hydroxyapatite-based substrate. Subsequently, adhesive performance of functional monomers, such as those containing dihydrogen phosphate or carboxylic acid, with HAp and dentin was studied.@footnote 3@ In this presentation, we will report chemical interaction analysis of functional monomer-hard tissue interfaces by utilizing high resolution XPS and relating analytical data. @FootnoteText@ REFERENCES:@footnote 1@ Y.Yoshida, B.Van Meerbeek, Y.Nakayama, J.Snauwaert, L.Hellemans, P.Lambrechts, G.Vanherle, K.Wakasa: J.Dent.Res., 79, 709 (2000).@footnote 2@ Y.Yoshida, B.Van Meerbeek, Y.Nakayama, M.Yoshioka, J.Snauwaert, Y.Abe, P.Lambrechts, G.Vanherle, M.Okazaki: J.Dent.Res., 80, 1565(2001) .@footnote 3@ Y.Yoshida, K.Nagakane, R.Fukuda, Y.Nakayama, M.Okazaki, H.Shintani, S.Inoue, Y.Tagawa, K.Suzuki, J.De Munck, B.Van Meerbeek: J.Dent.Res., 83, 454(2004) .

9:20am **BI+SS-FrM4 Evaluation of Residues on Implant Surfaces by X-ray Photoelectron Spectroscopy*, V. Frauchiger,*** *R. Luginbuehl,* Dr. H.C. Robert Mathys Foundation

Success of modern implants does not depend on the proper material choice only, but also on the surface chemistry and the proper removal of the ubiquitous present surface contaminations. There are many contemporary analytical methods that permit the qualitative and quantitative analysis of picogram amounts, but only a few methods are suitable for a direct assessment without a special preparation of the implants or the chemical extraction of residues. We applied X-ray photoelectron spectroscopy to assess the cleanliness of osteosynthesis plates and hip endoprosthesis implants. In addition, specially designed test coupon surfaces were used to simulate different surface textures. The samples were soiled with exact amounts of two model process adjuvants (MPA). The first one was based on a mixture of organic compounds used in lubricants and cutting fluids while the second one contained inorganic particles used in blasting processes. The cleaning efficacy of an industrial cleaning process in aqueous media and with sonication was tested. Imaging XPS was applied to localize critical contamination on the surfaces and small area analysis was used to identify the organic residues. In addition to XPS, GC-MS and gravimetric analysis were carried out as complementary techniques. Principal component analysis was used to establish a sensitivity at the ng/cm@super 2@ level by calculating the ratio between the bulk implant material and the carbon or other MPA specific elements. Cleaning tests revealed that the organic residues are completely removed upon proper choice of cleaning conditions and detergents. Residual inorganic particles were found on many samples with a blasted surface texture. The particles were removed only by special treatment of the samples.

9:40am **BI+SS-FrM5 Characterisation of Analyte / Matrix Interaction for MALDI / TOF Targets Using Spatially Resolved X-ray Photoelectron Spectroscopy*, A.J. Roberts,*** *D.J. Surman, S.J. Hutton,* Kratos Analytical Ltd, UK*; M. Resch,* SDG, Germany*; E. Raptakis, O. Belgacem,* Kratos Analytical Ltd, UK

Matrix-assisted laser desorption/ionisation (MALDI) is now an established technique for mass spectrometry of proteins and peptides. Different matrix-analyte preparation protocols have been shown to influence the desorption or ablation process resulting in either high or low metastable fragmentation. It has been speculated that following laser ablation the velocities of the analyte and matrix can be regarded as a valuable and meaningful characteristic of the MALDI process. However, the interaction and distribution of the analyte with respect to the matrix is poorly understood. Here we present a study of the distribution of a fluorinated peptide as a function of matrix material using imaging x-ray photoelectron spectroscopy (XPS). Both the lateral and depth distribution is investigated to draw conclusions on the incorporation of the analyte in the matrix.

10:00am **BI+SS-FrM6 In Situ Sum Frequency Generation Characterization of Adsorbed Alpha-helical Peptides*, N.T. Samuel,*** University of Washington*; K. McCrea,* Polymer Technology Group*; L.J. Gamble,* University of Washington*; R.S. Ward,* Polymer Technology Group*; D.G. Castner,* University of Washington

Controlling and characterizing the structure of adsorbed biomolecules is important for applications in diagnostics, tissue engineering and nanobiotechnology. Our previous studies showed that peptides with well-defined sequences of lysine (K) and leucine (L) amino acids spontaneously adsorb onto hydrophobic substrates with an alpha-helix secondary structure. The present study characterizes the adsorption of the LK peptides onto the surface through two approaches - immersing the hydrophobic substrate through the air-water interface (AWI) and avoiding the AWI. When the LK peptide is adsorbed avoiding the AWI a time-dependent change in the amide I intensity is observed. However, X-ray Photoelectron Spectroscopy (XPS) analysis showed no significant time dependence of the nitrogen surface composition. Similarly, the CH region of the SFG spectrum shows no time-dependence. These results indicate that the amide I SFG spectrum follows the time-dependent ordering of the peptide molecules on the hydrophobic surface. Results from site-specific labeling of the alpha-helix LK peptide molecules with deuterated leucine residues showed it was possible to follow interactions of one amino acid residue of the peptides with the surface.

10:20am **BI+SS-FrM7 Molecular Level Studies on Interfacial Protein and Peptide Structures Using SFG*, Z. Chen,*** University of Michigan

Molecular structures of interfacial proteins and peptides play important roles in biocompatibility, anti-biofouling control, membrane protein function, and anti-microbial peptide behavior. Sum frequency generation (SFG) vibrational spectroscopy has been applied to investigate molecular structures of proteins and peptides at the solid/liquid interface in situ. A thin film model was adopted to interpret SFG spectra. Isotope labeled method was introduced in the SFG studies. SFG results demonstrate that C-H stretching and amide signals can elucidate structures of hydrophobic side chains and secondary structures of interfacial peptides and proteins respectively. Detailed correlations between SFG amide I signals and secondary structures of interfacial proteins and proteins have been deduced. Various peptides and proteins including several anti-microbial peptides, albumin, lysozyme, fibrinogen, and factor XII (FXII) have been studied. Time-dependent structural changes of adsorbed proteins at the solid/liquid interface have been monitored. In addition, SFG chiral spectra were collected from interfacial peptides and proteins, which provide additional measurements to determine structures of these proteins and peptides. We also showed that combinations of linear vibrational spectroscopy such as attenuated total reflection Fourier transform infrared spectroscopy with nonlinear vibrational spectroscopic techniques such as SFG and four-wave mixing provide more detailed structure of surfaces/interfaces than that from a single technique.

10:40am **BI+SS-FrM8 Using Ellipsometry and Textured Surfaces to Enhance Infrared Response of Adsorbed Biomaterials*, D.W. Thompson,*** *J.A. Woollam,* University of Nebraska-Lincoln

Infrared spectra are of interest for numerous applications because of the chemical bond information present in the absorption characteristics, but obtaining meaningful infrared spectra from monolayers adsorbed to surfaces can be difficult because of the small amount of material being probed. For instance, it is often of interest to probe adsorbates on a surface after exposure to a protein solution. Use of textured (patterned) surfaces to increase the mass of material sensed is expected to enhance these spectra. Here the infrared ellipsometric enhancement is calculated for a layer of adsorbate on a number of proposed nanostructured surfaces to predict which is most advantageous for obtaining infrared spectra. The approach used here could also be applied to other adsorbates by optimizing the pattern dimensions for different sizes. It also works for visible spectroscopy as long as pattern dimensions are significantly smaller than the wavelength. The effect of using these structures (rods, wells, and trenches) is compared to the response of flat metal or dielectric surfaces over a range of incidence angles of the infrared beam. Predicted sensitivities are based on the calculated effect of adsorbate on intensities in an ellipsometric measurement. Trench structures appear to have significant advantages both in sensitivity and ability to distinguish adsorbed species orientation.

11:00am **BI+SS-FrM9 Understanding the Elasticity of Fibronectin Fibrils: A Single Molecule Force Spectroscopy Study***, **N.I. Abu-Lail**, T. Ohashi, R. Clark, H. Erickson, S. Zauscher,* Duke University

Although fibronectin (FN) is considered to be one of the most important components of the extracellular matrix, the detailed mechanism of the elasticity of FN fibrils is still unknown. To investigate the molecular origin of FN fibril elasticity we performed single molecule force spectroscopy (SMFS) measurements on a recombinant 1-8FN-III protein construct that contained two green fluorescent protein (GFP) domains spliced in-between the 3FN-III and 4FN-III domains. The relative strengths of both domains were investigated over a wide range of pulling rates (50 nm/s to 1745 nm/s). FN-III domains were distinguished from GFP domains based on their characteristic unfolding distance signature. We found that the mechanical stability of both domains was similar and that the unfolding forces of both domains were linearly related to the logarithm of the pulling rate. An extrapolation of the unfolding forces to small pulling rates showed that the force required to unfold the FN-III domains and GFP domains were undistinguishable and on the order of physiological forces (~10 pN). Our results, combined with earlier fluorescence resonance energy transfer (FRET) studies performed on the same recombinant proteins, suggests (1) that the FN-III domains are most likely bent and looped into a compact conformation in the cell culture and (2) stretching extends their conformation while the domains remain mostly folded.

11:20am **BI+SS-FrM10 Protein-Solvent Interactions in Surface-Grafted ELPs Measured by Single Molecule Force Spectroscopy***, **A. Valiaev**, D.W. Lim, S. Schmidler, A. Chilkoti, S. Zauscher,* Duke University

Stimulus-responsive biomolecules attract significant research interest due to their potential applications in areas such as drug delivery, molecular motors and nanoscale sensors. Here we present our results of the conformational and hydration behavior of surface grafted elastin-like polypeptides (ELPs), measured by single molecule force spectroscopy. ELPs are stimulus-responsive polypeptides that contain repeats of the five amino acids Val-Pro-Gly-Xaa-Gly (VPGXG), where Xaa is a guest residue, and undergo an inverse phase transition in response to an environmental stimulus, such as a change in temperature. Our results suggest that single-molecule force spectroscopy can be used to quantify the effect of the type of guest residue, pH or ionic strength on molecular conformation and elasticity. By fitting ELP force-extension data to a freely jointed chain model, using our newly developed data analysis approach, we showed that we can resolve differences in Kuhn segment lengths as small as 0.03 nm; i.e., differences that are about an order of magnitude smaller than those previously reported. The observed force-extension behavior at intermediate and large extensions supports a phenomenological model that describes ELPs as kinetically mobile and disordered macromolecules. Importantly we find that molecular elasticity upon extension arises both from a deformation of the polypeptide backbone and from hydrophobic polymer-solvent interactions. Our observations here agree with recent MD simulations which suggest that hydrophobic hydration of side-chains plays an important role for elasticity and provides the molecular basis for the inverse temperature transition behavior.

11:40am **BI+SS-FrM11 Developments of Flexible Tethers to Measure Antibody-Antigen Interactions using AFM***, **Z. Suo**, F. TerÃ¡n Arce, R. Avci, E. Smith, K. Thiltges, B. Spangler,* Montana State University

Functionalization of an AFM tip surface with covalently bound flexible tether molecules is of special interest because such a flexibility is necessary to measure, in a controllable fashion, the receptor-ligand binding events in the physiological environment of the biomolecules. However, the interpretation of the experimental data is often obscured by and confused with the nonspecific binding events between the substrate surface and the so functionalized AFM tip. Effective methods must be developed to eliminate and/or to identify these nonspecific binding events. To achieve these objectives we employed low densities of varying-length poly(ethylene glycol) (PEG) units grafted onto gold-coated AFM tip surfaces. These tethers were covalently linked to the antibodies of interest, in this case anti-cytochrome c. It was necessary to pacify the uncovered portions of the AFM tip in order to block the nonspecific tip-surface interactions. This was achieved by using the flowers-in-the-meadow concept: by mixing a self-assembled monolayers of small molecular size hydroxyl-terminated PEG unit (meadow) with the specifically terminated larger molecular size PEG unit (flower) as described above. AFM force-extension measurements using such a tip conducted on mica substrate covered with cytochrome c resulted in force and length distributions which are consistent with the tether lengths employed. The pH value and the ionic strength of the buffer have considerable influence on the binding events between the AFM tip and the surface covered with cytochrome c. We will present results covering these topics as well as the role of the coupling chemistry between the end terminals of a PEG molecule and the anti-cytochrome c and the AFM tip on the efficiency of antibody-antigen recognition events.

Electronic Materials and Processing
Room 309 - Session EM-FrM

Organic Electronic Devices

Moderator: A. Kahn, Princeton University

8:20am **EM-FrM1 Charge Transport in Amorphous Organic Semiconductors : Can We Describe a Wide Variety of Devices by a Single Model?***, **Y. Roichman**,* Princeton University **INVITED**

During the last years we witnessed an improvement of organic electronic devices and emergence of new devices, as a homogenous PN junction. At the same time the theory of charge transport in organic semiconductors was reexamined, with an emphasis on application to devices realistic operation condition. In this talk I will review the recent experimental evidences and advances in theory of charge transport in amorphous organic semiconductors. I will demonstrate that taking into account non-linear effects and a reasonable shape density of states the electronic behavior different devices (PN homogenous diode, PV cell and FET) that operate at different conditions can be explained by a single theoretical model. The differences between the major theoretical approaches will be briefly discussed as well.

9:00am **EM-FrM3 Physical Mechanisms in Programmable Nanoscale Organic Nonvolatile Memory Devices***, **T. Graves-Abe**, J.C. Sturm,* Princeton University

Great interest in novel, low-cost memory technologies has led to the development of a number of promising approaches based on organic thin films.@footnote 1@ We have recently reported memory devices based on 10-nm self-assembled films of 11-mercaptoundecanoic acid (MUA) sandwiched between gold electrodes.@footnote 2@ Devices can be placed into a high-conductance "ON" state by 3- to 4-V pulses and returned to a low-conductance "OFF" state with higher-voltage pulses. Devices have a number of desirable characteristics, including durability (more than 10@super 4@ write/erase cycles without degrading), nonvolatile memory states, fast programming times (<@micro@s), and large current densities (up to 10@super 5@ A/cm@super 2@ at 1 V) to minimize resistance-capacitance delays in large memory arrays for fast access times. Models based on charge-trapping or conducting-path formation have been proposed to describe similar results in other thin films,@footnote 3@ although in practice it is difficult to distinguish between the models. In this work, we report strong evidence that the programmable conductance of our devices is due to the formation and destruction of conductive paths. This evidence includes: i) the presence of multiple step-like increases in current during the transition from OFF to ON states, which are attributed to the formation of a small number (<10) of conducting paths leading to the ON state, ii) the exponential reduction in the time required to form these conductive paths with increased electric field, consistent with the field-assisted diffusion of metal ions into the organic layer to form the paths, iii) the dependence of electrical characteristics on choice of electrode material, and iv) the extremely thin nature of the films. @FootnoteText@ @footnote 1@ Y. Yang et al, MRS Bull. 29, 833 (2004).@footnote 2@ T. Graves-Abe and J. C. Sturm, Mat. Res. Soc. Symp. San Fran., CA, April 2005.@footnote 3@ G. Dearnaley et al, Rep. Prog. Phys. 33, 1129 (1970).

9:20am **EM-FrM4 Effect of Poly (3-hexylthiophene) Film Thickness on Organic Thin Film Transistor Properties***, **H. Jia**, S Gowrisanker, G.K. Pant, R.M. Wallace, B.E. Gnade,* University of Texas at Dallas

We present the effect of poly (3-hexylthiophene) thickness on the performance of OTFTs. When the poly (3-hexylthiophen) film thickness varies from 3.8nm to 23.8nm, the drain current and the saturation mobility increase with the thickness because of the higher channel conductance. In contrast, the on/off ratio decreases with P3HT film thickness, primarily because of the higher off current. Gate leakage also becomes higher when the film thickness increases, also contributing to a lower on/off ratio. The threshold voltage is more sensitive to dielectric surface treatment than to the thickness of P3HT film thickness. The mobility increases and then saturates with gate voltage. For devices from thick P3HT films, increasing gate voltage further after saturation decreases the mobility. Short channel effects are observed for channel lengths of @<=@ 5 µm. We also present the channel length dependence of threshold voltage and mobility. The drive current, on/off ratio, and mobility of P3HT devices should be optimized based on the specific application. @Footnote Text@@footnote 1@ Jiyoul Lee, Kibum Kim, Jae Hoon Kim, Seongil Im, Duk-Young Jung, Appl. Phys. Lett. 82, 4169 (2003) @footnote 2@ Satoshi Hoshino, Toshihide Kamata, and Kiyoshi Yase, J. Appl. Phys. 6028 (2002) @footnote 3@ R. Schroeder, L. A. Majewski, and M. Grell, Appl. Phys. Lett. 83, 3201 (2003) @footnote 4@ Manabu Kiguchi, Manabu Nakayama, Kohei Fujiwara, Keiji Ueno, Toshihiro Shimada and Koichiro Saiki, Jpn. J. Appl. Phys. 42, L1408(2003)

9:40am **EM-FrM5 Vapor and Solution Deposited Organic Thin Film Semiconductor Transistors***, **T.N. Jackson,*** Penn State University **INVITED**

Organic thin film transistor (OTFT) device performance now rivals or exceeds that of a-Si:H devices, and low OTFT process temperatures allow fabrication on a range of surfaces including cloth, paper, or polymeric substrates. However, it is still unclear whether OTFTs will find significant commercial application. To do so, OTFTs must demonstrate characteristics that differentiate them from other device technologies, especially a-Si:H TFTs. Potential advantages for OTFTs include the possibility of device and system fabrication on substrates not readily accessible to a-Si:H devices and also reduced cost manufacturing. For practical device and system use, OTFTs must demonstrate the uniformity, reproducibility, reliability, and integration with other devices, needed for realistic applications. As a candidate application we have considered the integration of vapor-deposited OTFTs with organic light emitting diodes (OLEDs). Working with Kodak we have fabricated small test displays that allow us to investigate device characteristics and passivation and isolation requirements for integrating these organic devices. Solution-deposited organic semiconductors may offer important advantages for low-cost processing. However, solution processed semiconductors typically lack the molecular-level order which may be important for good carrier transport and large field-effect transistor mobility. Working with J. Anthony (University of Kentucky) we have investigated functionalized pentacenes and pentacene derivatives. These materials use bulky molecular side groups to control molecular packing and allow solubility in a range of common solvents. Surprisingly, solution-deposited films of some of these materials show good molecular ordering and using these materials we have been able to fabricate OTFTs with mobility > 1.5 cm@super 2@/V-s.

10:20am **EM-FrM7 Optical and Electrical Properties of a New N-type Semiconductor: N, N@super '@-bis (3-phenoxy-3-phenoxy-phenoxy)-1,4,5,8-naphthalenetetracarboxylic diimide***, **D.X. Yang**, R.P. Shrestha,* University of North Carolina-Chapel Hill*; T.J. Dingemans,* Delft University of Technology, The Netherlands*; E.T. Samulski, E.A. Irene,* University of North Carolina-Chapel Hill

Optical properties of N, N@super '@-bis (3-phenoxy-3-phenoxy-phenoxy)-1,4,5,8-naphthalenetetracarboxylic diimide (NDA-n2) thin film, a N-type organic semiconductor, were investigated using optical transmission and spectroscopic ellipsometry (SE) in the visible-near uv optical range. The dispersion in refractive index and extinction coefficient along with anisotropy, surface roughness and annealing results are reported. An oscillator model with one Tauc-Lorzentzian oscillator and four Gaussian oscillators was proposed to describe the dielectric function of NDA-n2. Vacuum annealing of the thin film was performed and monitored using in-situ SE. The films we stable up to 150 °C and no optical anisotropy was found for the films. Capacitance versus voltage (C-V) and current versus voltage (I-V) measurements were performed on capacitor and thin film transistor (TFT) structures, respectively. The C-V results indicate a value of about 3.4 for the static dielectric constant. The I-V yields TFT transfer characteristics that are used to optimize the film formation process and device performance of the thin film semiconductor for TFT@super '@s. The mobility of NDA-n2 was obtained from I-V results in a TFT structure.

10:40am **EM-FrM8 Growth and Chemical Structure of Crystalline Rubrene Films***, **G. Witte**, D. Kaefer, Ch. Woell,* Ruhr-University Bochum, Germany

Rubrene single crystals have recently been demonstrated to exhibit remarkably high charge carrier mobilities@footnote 1@ which favors the use of this organic semiconductor material for molecular electronics applications e.g. organic field effect transistors. In contrast to other oligomer semiconductors such as pentacene the growth of crystalline thin films, however, has not been achieved for rubrene. Using x-ray absorption spectroscopy (NEXAFS) we have analyzed the initial stage of film growth on various substrates and demonstrate the importance of molecular conformation which involves a loss of chirality in case of rubrene. Whereas organic molecular beam deposition at room temperature only leads to rather amorphous layers, dendritic films are obtained at high substrate temperatures but the size of the crystallites is mainly limited by competing dewetting and desorption. An improved crystallite growth is achieved by using a modified "hot wall"-type deposition cell which allows operation under UHV-conditions but at much higher vapor pressure. Moreover, by combining AFM and SEM with XPS and LDI-TOF mass spectroscopy the morphology of the films and the amount of rubrene-peroxide formed upon exposure to air was characterized. Large differences in the corresponding rubrene-peroxide concentrations and their depth profiles were found for the various films and crystals which is of great importance for applications in molecular electronics. @FootnoteText@@footnote 1@ V.C. Sundar et al. Science 303, 1644 (2004).

11:00am **EM-FrM9 Pentacene Wetting Layer Formation on SiO@sub 2@ Substrate***, C. Kim, **D. Jeon,*** Seoul National University, South Korea

We have applied in-situ ellipsometry to study the growth of pentacene film on the SiO@sub 2@ surface. As soon as the evaporation began, the intensity of ellipsometry spectrum decreased. Atomic force microscopy (AFM) images of the early stage of growth, however, did not show any pentacene-related morphology. The pentacene islands in the first layer appeared after a continued deposition. The immediate change of ellipsometry spectrum with the onset of deposition indicates that pentacene molecules accumulate on the SiO@sub 2@ surface from the beginning. However, the flat AFM image of the early stage indicates that pentacene initially forms an amorphous wetting layer before crystalline islands appear. The roughness of the SiO@sub 2@ surface decreased with the pentacene deposition, which is another indication of the amorphous wetting layer. Pentacene is known to form a wetting layer on a clean metal or semiconductor substrate. In other words, pentacene reacts with the surface before a crystalline film forms. Our result shows that pentacene forms a wetting layer on an inert substrate as well. The existence of an amorphous layer on an insulating substrate should affect the performance of the pentacene devices. To show this we will also present the result from the electrostatic force microscopy of the pentacene film. This work was supported by the Nano Systems Institute at Seoul National University.

Magnetic Interfaces and Nanostructures
Room 204 - Session MI+BI-FrM

Biosensors and Biomagnetism

Moderator: D.P. Pappas, NIST-Boulder

9:00am **MI+BI-FrM3 Engineered Magnetotactic Bioreporter Bacteria@footnote 1@***, **L.J. Whitman,*** Naval Research Laboratory **INVITED**

There is an urgent need for compact, low power, broad spectrum sensors for sentinel point detection of toxins and pathogens. Although cell-based sensors have the potential to meet many of these requirements, it is a challenge to make such systems deployable because of the fragility of most cell cultures and the short lifetime of most bioreporter cells. We are addressing these issues by developing a robust, microbial sensor based on a strain of magnetotactic bacteria, Magnetospirillum magneticum AMB-1, that naturally produces an intracellular chain of magnetite nanoparticles (magnetosomes). We have produced a variety of genetically engineered AMB-1, including magnetic knockouts, with the goal of creating a reporter strain that only produces magnetosomes in the presence of specific toxic industrial chemicals. Wild-type and engineered strains have been extensively characterized by a variety of physical and chemical methods. We have determined that magnetosome production can be a rapid process, occurring in minutes, and that iron uptake correlates well with the measured magnetic moments. To rapidly determine when magnetosomes are present in the live cultures, a miniature optical system has been developed that detects differential light scattering from magnetically-aligned bacteria. Because stable populations of AMB-1 can be maintained for weeks under a range of environmental conditions, this organism appears to be a promising candidate for cell-based sentinel point detection. @FootnoteText@ @footnote 1@This work was done in close collaboration with M. B. Johnson, A. Krichevsky, J. C. Rife, M. J. Smith, C. R. Tamanaha, and R. J. Tonnuci at NRL, and B. M. Applegate, L. N. Csonka, L. K. O'Connor, and L. Perry at Purdue University. Supported by DARPA BioMagnetICs.

9:40am **MI+BI-FrM5 Synthesis and Surface Engineering of Superparamagnetic Nanoparticles***, **R. De Palma**, S. Peeters, K. Bonroy, G. Reekmans, F. Frederix, W. Laureyn, G. Borghs, C. Van Hoof,* IMEC vzw, Belgium*; G. Maes,* KULeuven, Belgium

Superparamagnetic nanoparticles with appropriate surface chemistry have been widely used for numerous applications such as MRI, hyperthermia treatment, magnetic biosensing, etc. These applications require that the nanoparticles have high magnetization values, a well-defined and controllable morphology and an overall uniform size distribution. In addition, these applications need special (bio)chemical functionalisation of the magnetic nanoparticles, specifically tuned towards their demands. Most work has been done in improving the quality of magnetic nanoparticles, but only a few scientific investigations have been carried out in engineering and improving their (bio)chemical surface characteristics. Here we present several approaches, to engineer the surface characteristics of superparamagnetic nanoparticles, without altering their magnetic and morphological characteristics. Monodisperse superparamagnetic nanoparticles with controllable size, shape and magnetic properties were synthesized based on the thermal decomposition method. The chemical functionality of these nanoparticles could be tuned by the covalent attachment of thin silane SAMs on the particle surface. An optimized procedure allowed the controllable deposition of high quality silane SAMs with different endgroups. By these means, the nanoparticles could be made water-soluble and capable to covalently couple biological receptors. Several receptors were successfully immobilized onto magnetic nanoparticles, while retaining their biological activity. The degree of receptor immobilization was determined to be 2-10 times higher, compared to 2D substrates. The synthesized magnetic nanoparticles were also coated with a thin shell of inorganic material such as Au and SiO@sub 2@ based on a novel and straightforward coating procedure. The superparamagnetic nanoparticles were characterised using TEM, XRD, FTIR, XPS, UV/vis, SQUID and Bradford.

10:20am **MI+BI-FrM7 Shaken Not Stirred, A New Approach to Biomagnetic Sensing***, **A. Hoffmann**, S.-H. Chung, K. Guslienko, S.D. Bader, C. Liu, B.D. Kay, L. Makowski, L. Chen,* Argonne National Laboratory **INVITED**

Micron and nanosized magnetic particles coated with biochemical surfactants have emerged recently as an important component for enabling many biological and medical applications. Among these biomagnetic sensors have received a lot of attention lately, due to their potential advantages of simplicity and rapidity. The most common approach to biomagnetic sensors utilizes magnetic beads, whose magnetic moment is detected by a magnetic field sensor, such as a giant magnetoresistive spin valve. In contrast we demonstrated a new substrate-free approach to biomagnetic sensing which uses the magnetic ac-susceptibility of ferromagnetic nanoparticles suspended in a liquid for the signal transduction.@footnote 1@ The magnetic relaxation of these nanoparticles is due to their Brownian rotational diffusion, which is easily modified by binding the target of interest to the particles. This scheme has several distinct advantages; (i) it requires only one binding event for successful sensing; (ii) since there is a useful signal both in the absence and presence of the target it has an inherent check for integrity; and (iii) the signal contains information about the size of the target besides the biochemical affinity, which may be used to further distinguish between several different potential targets. We are developing novel magnetic viruses for application in our sensing scheme. They provide a well-defined, mono-dispersed size distribution of the ferromagnetic particles and offer the possibility to readily engineer the desired biological recognition functionality. This work was supported by DOE, BES under contract W-31-109-ENG-38 and DARPA under contract 8C67400. @FootnoteText@ @footnote 1@ S.-H. Chung, et al., Appl. Phys. Lett. vol. 85, 2971 (2004).

Nanometer-Scale Science and Technology
Room 210 - Session NS-FrM

Nanotube Processing and Properties

Moderator: N.A. Burnham, Worcester Polytechic Institute

8:20am **NS-FrM1 Precise Placement of a Multi-Wall Carbon Nanotube using Nano Manipulator in SEM***, **H. Abe**, M. Tanaka, M. Horikawa, Y. Naitoh, T. Shimizu,* AIST, Japan

There have been many studies for realizing electric devices using carbon nanotubes (CNTs). Particularly a variety of growth methods have been developed in order to control the diameter and the electric properties. In addition, we have thought that it is important to place precisely a CNT onto the designated position and make electrically and mechanically reliable contacts between CNT and electrodes for the realization electric circuit using CNT. From now, we have manipulated a multi-wall CNT (MWNT) and fabricated a MWNT tip for high-resolution SPM measurement using specially designed SEM manipulator. Then we developed several bonding methods by melting low melting point alloy and TiNi nano particles, whose bonding showed good conductivity of several 10k@ohm@ and mechanical strength of more than 2GPa. In addition to the techniques, we have tried to fabricate a bridge structure using a MWNT in the SEM manipulator. Then we succeeded in bridging a MWNT between electrodes whose distance is from 1µm to 4µm. This technique enables us to control the attaching position of less than 50nmx50nm and to float or touch MWNT from the substrate. We could really bridge a MWNT by floating between thermal heater of 300nm and thermal bath for precise thermal conductivity measurement of a single MWNT. We have thought that this technique could be applied to other nanotubesâ?T bridge structure fabrication and their physical property. The way of fabricating a MWNT bridge structure will be shown using video file in detail in our presentation.

8:40am **NS-FrM2 Hydrogenation of Single Wall Carbon Nanotubes***, **A.S. Nikitin**, H. Ogasawara,* Stanford Synchrotron Radiation Laboratory*; D. Mann, Z. Zhang, H. Dai, K.J. Cho,* Stanford University*; A. Nilsson,* Stanford Synchrotron Radiation Laboratory

The hydrogenation of the single wall carbon nanotubes (SWCN) is considered as a mechanism of hydrogen storage in the nanotube materials. We present the hydrogenation of the single wall carbon nanotube films with an atomic hydrogen beam. Using X-ray absorption spectroscopy, we demonstrated that C-C bonds in the walls of SWCN decrease of sp@super 2@ character and increase of sp@super 3@ character simultaneously due to hydrogenation. On the basis of X-ray photoelectron spectroscopy results combined with theoretical calculations, we show 65+/-15% hydrogenation of carbon atoms in the SWCN films that corresponds to 5.1+/-1.2 wt % hydrogen weight capacity of the studied sample. The formed C-H bonds are stable at ambient temperature and can be broken in the temperature range from 300°C to 600°C. These results clearly demonstrate that a chemical interaction mechanism of hydrogen with SWCN is possible with a large hydrogen storage capacity.

9:00am **NS-FrM3 Well - Aligned Growth of Carbon Nanotubes/Fibers in Anodized Aluminum Oxide Pores by DC Plasma Enhanced Hot Filament Chemical Vapor Deposition***, **H.W. Yap**, B. Ramaker, A.V. Sumant, R.W. Carpick,* University of Wisconsin-Madison

In many carbon nanotube (CNT) or carbon nanofiber (CNF) applications - such as field emission flat panel displays, it is ideal to have an ordered and dense vertically aligned dense CNT/CNF array over a large area. The anodized aluminum oxide (AAO) template is favorable since it offers uniformly spaced pores for isolated and directional growth of these CNT/CNFs. Several research groups have already reported the use of the AAO template to grow CNT/CNFs via thermal chemical vapor deposition (CVD) but they were not successful in obtaining vertical and isolated growth once they emerged from the pores. Thus, etching of the AAO had to be subsequently performed. Microwave plasma enhanced MPECVD has been shown to give better alignment, however it is not cost effective in terms of power requirements and large area deposition. Here we report a cost effective, low power alternative approach: dc plasma enhanced hot filament CVD (dcPEHFCVD). To our knowledge, this is the first successful report to grow well aligned CNTs via AAO pores using dcPEHFCVD. Here, no anodization of the aluminum, pore widening of the AAO, post growth etching of the AAO or pretreatment of the catalyst are needed. Nickel nanowires electrodeposited in the pores act as catalysts. We find that tip growth mode is dominant here. The hot filament plays an important role in dissociating hydrocarbon species as well as heating the substrate to enhance the catalyst driven CNT/CNF growth. The plasma's electric field aligns the CNT/CNFs and is responsible for most of the growth chemistry. High resolution transmission electron microscopy reveals that both CNTs and CNFs are formed via the tip growth mode and have graphitic walls. The majority of CNTs have hollow interiors but some CNFs exhibit herringbone - like fringes in the interior. AFM images of the tubes are obtained and provide quantitative measurement of the length variations of the tubes.

9:20am **NS-FrM4 Carbon Nanosheets--A Sub-nanometer Two-dimensional Carbon Nanostructure***, **M.Y. Zhu**, J.J. Wang, X. Zhao, R.A. Outlaw, B. French, D.M. Manos, B.C. Holloway,* College of William and Mary

In this paper, we report a sub-nanometer scaled two-dimensional carbon nanostructure--Carbon nanosheets (CNS) by radio-frequency plasma enhanced chemical vapor deposition (RF-PECVD). CNS were synthesized from mixed gases of methane (CH@sub 4@) and hydrogen (H@sub 2@) on various substrates, including Si, SiO@sub 2@, Al@sub 2@O@sub 3@, Mo, Zr, Ti, Hf, Nb, W, Ta, Cu and 304 stainless steel, without any catalyst or substrate pre-treatment. SEM, HRTEM, SAD, Raman spectroscopy, XRD, XPS and AES, were used to characterize the morphology and structure properties of the CNS. The results showed that CNS consist of graphene layers, oriented nearly vertically to the substrates. Typical CNS are hundreds of nanometers in width and height, but only few nanometers in thickness, sometimes as thin as a single-atomic-layer. Raman spectra of CNS featured D peaks and G peaks for sp@super 2@ bonded carbon, and low energy peaks, similar to RBM mode of single wall carbon nanotubes, were also observed. Analysis indicated that CNS is pure carbon without detectable contamination. BET measurement revealed a specific surface area of ~1300m@super 2@/g, which is the theoretical maximum value for a 2-layered graphene sheet. The high surface area makes CNS a potential candidate of catalyst support and hydrogen storage in fuel cell applications. Diode I-V curves, acquired to study the field emission property of nanosheets, showed a turn-on field as low as 1 V/µm and a current density of 2.2mA/mm@super 2@ over an area of 1mm@super 2@. This indicates that CNS is a good cathode material for cold field emission devices.

9:40am **NS-FrM5 Super Growth - Highly Efficient Synthesis of Impurity-Free Single-Walled Carbon Nanotubes and its Applications***, **K. Hata**,* AIST, Japan **INVITED**

We demonstrate an extremely efficient chemical vapour deposition synthesis of single-walled carbon nanotubes where the activity and lifetime of the catalysts are enhanced by an addition of water into the ambient of the CVD furnace, a growth mode we call "Super Growth".@footnote 1@ The enhanced catalytic activity of super growth results in massive growth of super-dense and vertically-aligned single-walled nanotubes forests with heights up to 2.5 millimeters. In addition, these SWNT forests were easily separated from the catalysts, producing the most pure SWNT material (over 99.98%) ever made, amazingly through an all-dry process without any purification. Moreover, patterned highly organized intrinsic single-walled nanotube structures were successfully fabricated. Super Growth simultaneously addresses many critical problems such as scalability, purity, and cost, and opens up innumerable opportunities ranging from fundamental research to real applications. @FootnoteText@ @footnote 1@K. Hata, et al.,Science 306. 1362 (2004)

10:20am **NS-FrM7 Microstructural Modifications of Multiwalled Carbon Nanotubes by keV Ar@super +@ Bombardment: a High Resolution TEM Study***, **D.-Q. Yang**, E. Sacher,* Ecole Polytechnique of Montreal, Canada

The surface functionalization and microstructural modification of carbon nanotubes (CNTs) have both attracted great interesting because of their potential applications to microelectronic devices and advanced functional CNT-based materials. One functionalization method is to break C-C bonds with keV Ar+ treatment, thus producing highly localized amorphous regions containing free radicals capable of further reaction. Such treatment of NTs has recently been found capable of changing the electronic properties and enhancing the field emission of multiwalled CNTs (MWCNTs). To better understand the interaction between the ion beam and CNTs, we have studied their microstructural evolution, under keV Ar+ beam irradiation, by high resolution TEM. We found that Ar+ treatment doses from 1013 to 1015 ions/cm2 produce free radical defects, an amorphous layer, as well as nanonodules that continue to grow and, on contacting another such growing nodule, crosslink the nanotubes. We discuss the formation mechanism of these microstructural modifications.

10:40am **NS-FrM8 Structural, Optical, and Electrical Properties of Functionalized SWNTs with DNA and Metal Nanoparticles***, **G.-H. Jeong**,* NTT Basic Research Laboratories, Japan*; A. Yamazaki,* Tokyo University of Science, Japan*; S. Suzuki, Y. Kobayashi, K. Furukawa, K. Torimitsu,* NTT Basic Research Laboratories, Japan*; Y. Homma,* Tokyo University of Science, Japan

Because of the outstanding physical, chemical and electrical properties of carbon nanotubes (CNT), a number of applications in various fields are expected. Especially, extensive CNT-functionalization researches have been performed to control electronic property because diameter- or chirality-controlled growth has not realized yet. Recently, we have performed the experimental approach to create CNT-based novel hybrid structures and demonstrate here the results. DNA and Au nanoparticles (NP) are selected to functionalize CNT due to their specific assembling property. By controlled chemical vapor deposition, single-walled carbon nanotubes (SWNTs) were successfully synthesized not only on flat substrate but also on Si-pillar substrate which allows suspending nanotubes. SWNTs-functionalization was performed by covalent coupling between carboxyl and amine groups. DNA/Au hybrids were made using thiolated-DNA and Au NP and confirmed by UV-visible absorption spectroscopy. Finally, SWNTs were modified with Au NP or DNA/Au hybrids. The density of Au NP attached along the suspended SWNTs was controlled by changing treatment time and concentration of the Au colloid. In Raman characterization, we observed new peaks at radial breathing band after Au NP attachment, which may be caused by surface-enhanced Raman scattering. Photoluminescence peaks were also detected from the SWNTs/Au hybrids and will be investigated the effect of Au functionalization. The intensity change of radial breathing band and defect band in Raman spectra was also observed from the SWNTs/DNA/Au hybrid, which implies the different electronic or optical properties are expected. These results show functionalized CNT can be further developed to electronic and optical applications. @FootnoteText@ @footnote 1@NTT Basic Research Laboratories, NTT Corporation, Atsugi, Kanagawa 243-0198, Japan @footnote 2@CREST, JST, c/o Dept. of Physics, Tokyo University of Science, Tokyo 162-8601, Japan

11:00am **NS-FrM9 Nanomechanical Resonance Studies of Carbon Nanotube Peapod Bundles***, P. Jaroenapibal, C.Y. Nam, J.E. Fischer, D.E. Luzzi,* University of Pennsylvania*; **S. Evoy**,* University of Alberta, Canada

The recent development of hybrid carbon nanotube materials, such as supramolecular self-assembled arrays of C60 molecules encapsulated within single-wall carbon nanotubes (C60@@SWNT), has opened new possibilities for the development of nanomechanical devices of tunable properties. We studied the mechanical properties of C60-filled SWNT bundles through analysis of their resonance in a transmission electron microscope (TEM). X-Ray diffraction was used to qualitatively study the filling of C60 in the bulk material. The intensity of the (1,0) bundle peak, located at Q = 0.45 A^-1, was reduced after filling of the tubes with C60. Electron diffraction analysis revealed a C60 spacing periodicity of 9.97 Ã. within the lumen of the SWNTs. Mechanical resonance measurements were conducted in a TEM by selecting bundles whose extremities were appropriately affixed. An average ratio of (E*/rho)^1/2 = 19002 Â± 2307 m/s was extracted from the resonance analysis of the C60-filled bundles, compared to a ratio of (E*/rho)^1/2 = 13230 Â± 3187 for the unfilled material. These values correspond to an effective average Young's modulus of E* = 240 Â± 105 GPa for empty bundles, and of up to E* = 650 Â± 156 GPa for the C60-filled materials. These moduli are significantly lower than the ~ 1 TPa usually reported for individual SWNTs due to the weak interaction and sliding effect that are known to exist between tube surfaces. However, the significant increase of stiffness upon filling is believed to be related to an increase of strain energy of the individual SWNTs within the bundle. A dependence of this modulus on bundle diameter was also observed. This dependence is explained by the increased importance of inter-tube slipping in bundles of larger diameter. We will also present recent results on the mechanical resonance properties of single-crystalline GaN nanowires. Preliminary resonant analysis of 30-160 nm wide wires suggest an average effective Young's modulus of E* = 120 Â± 20 GPa.

11:20am **NS-FrM10 Molecular Dynamics Simulation of Irradiation Effects on the Mechanical Failure of Multi-Walled Carbon Nanotubes***, **S.K. Pregler**, S.B. Sinnott,* University of Florida

Polyatomic ion-beam deposition on advanced materials, such as semiconductors, carbon nanotubes, polymers, and nanocomposites, to induce surface chemical modification is an important process used to achieve thin film growth, surface etching, and nano-texturing of the surface. Previous atomistic simulations have shown that particle beam deposition can induce crosslinking between the shells of unfunctionalized multiwalled carbon nanotubes. In this work, we investigate the effect of atomic, polyatomic, and electronic irradiation of chiral and armchair multiwalled carbon nanotubes. In particular, Ar and CF3+ ions are considered. The innermost shells of the irradiated nanotubes were then pulled at a constant rate of 40 m/s until axial load failure. The approach used is classical molecular dynamics simulations using reactive empirical bond-order potentials and the primary knock-on atom approach to model the effects of electron irradiation. The objectives of this study are to determine the degree to which multi-walled nanotube failure is mitigated by the irradiation-induced cross-links, and how irradiation affects the stability and structural integrity of the nanotubes. In addition, the influence of the irradiating species and nanotube chiral structure on the results is examined. Lastly, the predicted outcomes are compared to new and published experimental studies. This work is supported by the National Science Foundation (CHE-0200838).

11:40am **NS-FrM11 Direct Synthesis of Suspended Single-Walled Carbon Nanotubes Crossing Plasma Sharpened Carbon Nanofiber Tips***, C.H. Weng,* ***K.C. Leou****, W.Y. Lee, Z.Y. Juang, C.H. Tsai,* National Tsing Hua University, Taiwan

Single-walled carbon nanotubes are one of the most important quasi-one-dimensional nano-materials but their properties or associated device characteristics are very sensitive to the surroundings, e.g., surfactants or wrapping materials, and ambient gases, etc. It has been shown that such environmental perturbation effects could be minimized by suspending the SWNTs. Here we report a novel method for direct synthesis of suspended single-walled carbon nanotubes (su-SWNTs) using vertically-aligned carbon nanofibers (CNFs) as templates via a three-step fabrication process. Plasma enhanced chemical vapor deposition (PECVD) is first employed to grow vertically aligned CNFs on silicon substrates patterned with coated catalytic nickel film of 10 nm thickness. The CNFs are then post-treated by energetic argon plasma in the same reactor to yield structural transformation of CNFs with sharpening tips embedded with catalytic nanoparticles of a favorable size, presumably below 10 nm. A thermal CVD process then subsequently followed to directly synthesize SWNTs suspended across the tips or sidewalls of post-treated CNFs (PT-CNFs) with a span up to 10 µmm, as revealed by the analysis using scanning electron microscopy and resonance micro-Raman spectroscopy. We also demonstrated that one can maximize the yield of su-SWNTs on the tips of PT-CNFs by optimizing the post-treatment conditions to provide a protective coating to suppress the growth of SWNTs from sidewalls. The method of fabricating su-SWNTs described in this letter can be extended to position a single isolated SWNT for the purpose of either minimizing environmental perturbations during SWNT characterization or enhancing performance in nano-device applications.@footnote 1@ @FootnoteText@ @footnote 1@ This work was supported by the National Science Council of the Republic of China and the Center for Nano Science and Technology in the University System of Taiwan.

Plasma Science and Technology
Room 302 - Session PS-FrM

Plasma Surface Interactions III

Moderator: J. Caughman, Oak Ridge National Laboratory

8:20am **PS-FrM1 Flexible Organic Electronics: the Role of Plasma Deposition in Multi-Layer Permeation Barrier Technology***,* ***M. Creatore****, V.I.T.A. Lohmann, M.A. Blauw,* Eindhoven University of Technology, the Netherlands*; M.M. Koetse, H.F.M. Schoo,* TNO Science and Industry, the Netherlands*; M.C.M. Van De Sanden,* Eindhoven University of Technology, the Netherlands

The multi-layer system of alternated inorganic and organic layers is the state-of-the-art technology for flexible organic electronics where water vapor transmission rates down to 10@super -6@g/m@super 2@day are demanded. Under debate is the role of the organic layer, which appears crucial in affecting the growth of the inorganic film, as well as the multi-layer mechanical performance. In this framework, plasma technology has not been yet fully explored; however, it is expected to contribute to the improvement of a multi-layer system design because of the development (and, ultimately, the control) of a polymer/ inorganic layer interphase region. In this contribution we report on the studies performed by means of in situ real time diagnostics (e.g., spectroscopic ellipsometry) during the plasma deposition of inorganic (SiO@sub 2@) moisture barrier layers on polymers (poly(ethylene 2,6 naphtalate)), as well as during the growth of the organic (silicone-like) interlayer. The layers are deposited in an Ar-fed expanding thermal plasma, where the deposition precursors (hexamethyldisiloxane and oxygen) are injected downstream and negligible ion bombardment (< 2 eV) takes place at the substrate. In these conditions, a polymer/SiO@sub 2@ interphase region develops, attributed to a sub-surface polymer modification during the initial film growth by means of a non- depositing radical (O, OH) flux competitive with the depositing radical (Si, SiO) flux towards the substrate. The effect of ion bombardment (either delivered with an average ion energy or a narrow ion energy distribution), as provided by externally biasing the substrate, is also under investigation. Its effects on the interphase region as well as on the roughness evolution, both strictly related to the multi-stack moisture permeation and mechanical performances, will be addressed.

8:40am **PS-FrM2 Effect of Chamber Wall Condition for Organic Film Etching Using N@sub2@/H@sub2@ Plasma***,* ***K. Oshima****, T. Tatsumi, K. Nagahata, K. Shinohara,* Sony Corp., Japan

We investigated the relationship between N/H plasma and the wall conditions in a dual-frequency capacitively coupled plasma system. Organic low-k film is normally etched using N-H based plasma (N@sub2@/H@sub2@, NH@sub3@), which is difficult to control because the H radical density greatly depends on the chamber wall conditions. Obtaining an accurate critical dimension and suppressing damage induced by the plasma requires precise control of the low-k materials. We found that when Cu was redeposited on the chamber walls during stopper layer etching, the etch rate of the organic film was drastically decreased, presumably because the H radicals were immediately lost at the conductive surface. To clarify the reaction mechanism between H radicals and Cu, we analyzed the optical emission of H, N, and O in H@sub2@/Ar, N@sub2@/Ar, and O@sub2@/Ar plasma, respectively, with varying area ratios (Ra) of Cu on the Si wafer (from 1 to 100%). The emission of H clearly decreased with increasing Ra, while the N and O radical densities did not change. We also analyzed the reaction mechanism between C-F polymer and Si. When there was C-F polymer in the chamber, both O and H radicals showed relatively low density because the polymer consumed both spontaneously. Since N radicals need ion energy to react with C-F polymer, they have less dependency on the chamber wall conditions. After the polymer was cleaned with O@sub2@ plasma, the optical emission spectra intensity of H gradually decreased because the slight oxidation of the top electrode surface was reduced by H@sub2@ plasma exposure, and the conductive surface started to react with the H radicals. The wall conditions thus greatly affect the H radical density. Consequently, to realize stable processes, it is important to control both the generation of H radicals due to collisions between electrons and atoms or molecules and the loss of H radicals that react with the C-F polymer or metal on the chamber wall.

9:00am **PS-FrM3 Comparison of Hydrocarbon and Fluorocarbon Polyatomic Ion Beam Treatment of Polystyrene***, W.-D. Hsu, I. Jang,* ***S.B. Sinnott****,* University of Florida

Plasma processing is widely used to chemically modify polymer surfaces and deposit thin films. It is well-accepted that polyatomic ions and neutrals within low-energy plasmas have a significant effect on the surface chemistry induced by the plasma. Here, the detailed chemical modifications that result from of the deposition of beams of polyatomic fluorocarbon ions (C@sub 3@F@sub5@@super +@ and CF@sub 3@@super +@) and hydrocarbon ions (C@sub 3@H@sub 5@@super +@ and CH@sub 3@@super +@) on polystyrene surfaces at experimental fluences are identified using classical molecular dynamics (MD) simulations. The simulations make use of a reactive bond-order potential for hydrocarbons that has been extended to include fluorine and an optimized MD program. Based on the predicted accumulation of ion-surface collisions and accompanying chemistry, we elucidate how the unique chemical properties of the incident ions affect surface modification. We also determine the important differences and similarities in the chemical interactions of fluorocarbon and hydrocarbon ions with the polystyrene. This work is supported by the National Science Foundation through grant number CHE-0200838.

9:20am **PS-FrM4 Comparison of Surface Reactivity of CN, NH, and NH@sub 2@ Radicals during Deposition of Amorphous Carbon Nitride Films from r.f. Inductively Coupled Plasmas***,* ***D. Liu****, I.T. Martin, J. Zhou, E.R. Fisher,* Colorado State University

Carbon nitride films have received much attention because it has been proposed that the bulk modulus of @beta@-C @sub 3@N @sub 4@ may be greater than that of diamond. A number of groups have subsequently attempted to deposit carbon nitride films using various plasma techniques. However, the film deposition processes and their relationships with film properties are less studied. Here, the interactions of CN, NH, and NH @sub 2@ radicals with the carbon nitride film surface during r.f. inductively coupled plasma deposition were compared using the imaging of radicals interacting surface (IRIS) technique. Surface scattering coefficients, S, were obtained for various gas compositions of N @sub 2@+CH @sub 4@, and NH @sub 3@+CH @sub 4@, and r.f. powers. The S values of CN and NH radicals range from 0-0.15 and 0.8-0.9, respectively, and show very little dependence on the gas compositions and applied power. In contrast, the S values of NH @sub 2@ decrease from 0.8 ±0.1 to 0.4 ±0.1 when the CH @sub 4@ fraction in the plasma is increased. The essentially 100% scatter measured for NH suggests that NH is not a major deposition precursor in these plasmas. The effects of ion energies on S values were analyzed using DC bias of the substrate. The S values show an obvious dependence on the bias voltage. The r.f. inductively coupled plasmas during the film deposition have also been characterized during the film deposition by optical emission spectroscopy and mass spectrometry. Ion energy distributions were also measured using mass spectrometry. Results indicate that energetic ions are important in surface production of the species studied with IRIS. X-ray photoelectron spectroscopy analysis of deposited films showed the N content increases with increasing the N @sub 2@ or NH @sub 3@ fractions of reactive gases. The mechanisms for film deposition in these carbon nitride systems will be discussed in light of our gas-phase, surface, and gas-surface interface data.

9:40am **PS-FrM5 Real-time, Nonintrusive Monitoring of Drifting Ion Energy and Flux in a High-Density, Inductively Coupled Plasma Reactor***,* ***M.A. Sobolewski,*** National Institute of Standards and Technology

Measurements of the radio-frequency (rf) current and voltage applied to a plasma reactor, interpreted by plasma sheath models, provide an ability to monitor the total ion flux and ion energy distribution at surfaces inside the reactor. Such measurements are useful for monitoring drift in manufacturing or laboratory reactors when direct measurements of ion flux or energy are impossible or impractical. In this study rf measurements were used to monitor drift in Ar and Ar/CF@sub 4@ discharges in an inductively coupled, high-density plasma reactor. One source of drift in such reactors is the deposition of a conductive surface layer on the dielectric window of the inductive source. As this layer grows, a greater fraction of the source power excites currents in the layer, rather than in the plasma, resulting in less efficient operation and a reduction in plasma density and ion flux. These changes in turn affect the coupling of rf bias power into the discharge, producing changes in delivered rf bias power or voltage, sheath voltages, and ion energy distributions. Using rf measurements, the resulting changes in ion flux and energy were monitored in real time, as a surface layer was deposited. Changes in ion energies as large as 100 eV were observed. Increases as well as decreases in ion energies were observed, depending on rf bias conditions. Three different mechanisms that explain the changes in ion energies were identified. The application of the technique to monitoring process drift or irreproducibility caused by factors other than deposition on the dielectric window will also be discussed.

10:00am **PS-FrM6 Saturation of Etching Rate in Downstream Plasma Chamber Cleaning***,* ***J.J. An,*** *B. Bai, H.H. Sawin,* MIT

NF3 and fluorocarbon downstream plasmas were investigated to study downstream chamber cleaning system. As the flow rate of NF3 increases, the etching rate of TEOS increases; however, the etching rate saturated at a given sample temperature. Flamm (1979) showed the etch rate of fluorine is a linear function of the density of F atoms, but did not observe the saturation regime. Under chamber cleaning conditions, the etching rate can be saturated, particularly on the walls where the temperature is lower than in the electrode region. Therefore an understanding of this phenomenon is critical to understanding the rate limiting processes for chamber cleaning. The etching rate was modeled using a physisorbed precursor state in which atomic F is weakly bound to the surface. The physisorbed F reacted with the fluorinated surface in a sequential reaction with a particular reaction step being rate limiting. The reaction model gives the expected first order response with atomic F concentration that was observed by Flamm at low atomic fluorine concentrations in which the etching rate is limited by the combination of adsorption equilibrium and reaction rate. At sufficiently atomic F concentrations, the surface becomes saturated and the etching rate is limited by the surface reaction rate alone. Using these surface kinetics, a well mixed reactor model was used to compute the cleaning of chambers in which surface areas of differing temperatures are exposed to the same atomic F concentration. The results for this model will be discussed for both NF3 and fluorocarbon cleaning of PECVD reactors.

10:20am **PS-FrM7 Depletion of Plasma-Induced Charge on Semiconductor Dielectrics using Ultraviolet and Vacuum Ultraviolet Radiation***,* ***G.S. Upadhyaya,*** *J.L. Shohet, J.L. Lauer, R.W.C. Hansen,* University of Wisconsin-Madison

Radiation-induced charging during the processing of semiconductor materials can adversely affect device reliability. We have reported previously that vacuum ultraviolet (VUV) radiation with energies between 7-30eV can cause ionizing collisions in the dielectric creating charge carriers, thereby increasing the dielectric conductivity. However, the most dominant form of plasma-induced damage on a semiconductor dielectric is from electron and ion bombardment. As technology progresses, is more problematic because of increasing feature aspect ratios, Ions tend to collect at the bottom of high-aspect-ratio trenches while the lighter electrons crowd the trench walls, thus "shading" the ions. This electron-shading effect is not well documented due to the lack of a reliable diagnostic. In-situ techniques for depleting plasma-deposited charge will be an invaluable tool for manufacturing high quality devices. To this end, a technique for depleting plasma-induced charge by exposing plasma-charged wafers to either ultraviolet (UV) or VUV has been developed. Photons with energies ranging from 5-12eV possess sufficiently large penetration depths so as to photo-inject carriers from the substrate and thus deplete the previously deposited charge by conductive effects. Silicon wafers with silicon oxide or silicon nitride of thicknesses between 200 and 3000 Å grown on silicon were precharged to range of surface potentials of the order 4-10 volts by exposure to a 13.56 MHz RF plasma. The wafers were then exposed to synchrotron radiation with photon energies between 5-12 eV. From the comparison of the surface potential distributions before and after UV/VUV exposure, it is possible to determine the penetration depth of the VUV, the conditions for photoemission and photoconductivity, as well as the effectiveness of charge depletion as a function of photon energy and dielectric thickness. @FootnoteText@ Work supported by NSF under grants DMR-0306582. and DMR-0084402.

10:40am **PS-FrM8 Investigating the Interaction of High-Pressure, High Temperature Plasmas with Propellant Surfaces through Experimental Modeling***, R. Valliere, A. Dyachenko,* ***R. Blumenthal,*** Auburn University

The electrothermal chemical (ETC) ignition of propellants has many advantages over conventional ignition, the most remarkable is a short, highly-reproducible ignition delay. ETC ignition results from the impingement of a multi-millisecond long pulse of high-pressure, high-density atomic plasma on the surface of the propellant. The plasma is generated by the nearly complete ablation of a polymer tube as a large capacitor is discharged through it. Direct determination of the chemical and physical processes responsible for the beneficial properties of ETC ignition would require surface sensitive probes capable of penetrating a plasma pulse that has pressures up to 33 MPa and temperatures as high as 30,000 K.@footnote 1@ In the absence of suitable probes, one must find an alternative approach. An often overlooked alternative to direct measurement is experimental modeling, pioneered by Winters and Coburn.@footnote 2@ Experimental modeling consists of replacing a complex and/or impenetrable environment with one or more of its individual components, generated in a way that is compatible with traditional surface probes. In the study of plasma ignition, the challenge is to find a vacuum compatible replacement for the ETC source output. In this work, atomic plasmas with composition and pressures close to those of the plasma pulse are created by laser ablation of thin polymer films deposited directly on the surface of the propellant. The chemical products of the nanosecond-long plasma with the propellant surface are monitored by mass spectrometry and the resulting surface is examined by XPS and Auger with the results compared to those found after truncated ETC ignition. @FootnoteText@ @footnote 1@ M. Nusca, M.J. McQuaid and W.R. Anderson, J. Thermophys. Heat Trans. @bold 16(1)@,157 (2002).@footnote 2@ H.F. Winters, and J.W. Coburn, JVSTB @bold 3(5)@, 1376 (1985).

Surface Science
Room 202 - Session SS1-FrM

Surface Modification through Etching

Moderator: K.T. Queeney, Smith College

8:20am **SS1-FrM1 Creating Si Structures from Meso- to Nano-scale via Chemical and Laser-Assisted Methods***,* ***K.W. Kolasinski,*** University of Virginia **INVITED**

Nanocrystalline porous silicon is created by etching Si in fluoride solutions. The reaction is initiated by valence band holes that are provided by laser irradiation or suitable oxidants. The composition of the fluoride solution can be used both to elucidate the mechanism of etching as well as to control properties of the resulting microporous film. Several new classes of stain etchants - containing some combination of HF, NH@sub 4@HF@sub 2@, HCl, HNO@sub 3@, Fe(III), Mn(VII) and water - have been investigated. Once porosified, the films exhibit visible photoluminescence (PL). The peak PL wavelength depends on the etchant composition. Properties of the film, such as morphology, porosity and the PL maximum wavelength, respond to the etchant composition. Of particular interest is the observation of a blue shift in PL, which correlates with an increasingly positive electrochemical potential (E@sub 0@) of the oxidant. It is argued that E@sub 0@ plays a role much like wavelength in photoelectrochemical etching and that smaller nanocrystals are produced with more positive values of E@sub 0@. Micrometer scale Si pillars are formed by chemically enhanced laser ablation using nanosecond excimer laser irradiation (308 nm, ~3 J cm@super -2@) of Si in the presence of SF@sub 6@. Smaller pillars are formed using femtosecond irradiation (790 or 390 nm, ~ 1 J cm@super -2@). We can control the initiation of precursor holes by ruling a grating into the Si substrate prior to irradiation. Near-field amplification of the laser intensity enhances the formation of the precursor holes and aligns them parallel to the rule. Continued irradiation leads to the break up of the holes into pillars. The pillars can be thinned and eventually removed by wet chemical etching in aqueous KOH resulting first in ordered arrays of pillars with aspect ratios approaching 10,000 (e.g. tens of microns in length, with ~10 nm tips) and then macropores. Macropore shape is determined by crystallography and the anisotropy of the wet etchant.

9:00am **SS1-FrM3 Optical Second Harmonic Generation as a Diagnostic Tool in Ar@super +@ and XeF@sub 2@ Beam Etching Studies of Silicon***, **J.J.H. Gielis**, A.A.E. Stevens, P.M. Gevers, H.C.W. Beijerinck, M.C.M. Van De Sanden,* Eindhoven University of Technology, The Netherlands*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands

Insight into surface and interface properties during plasma etching of micro- and nanostructures is essential to obtain optimal device performance. In this work we study surface and interface processes during etching of Si by implementing the surface and interface sensitive nonlinear optical technique of second harmonic generation (SHG) in a UHV multiple-beam experiment including an Ar@super +@ ion gun and a XeF@sub 2@ beam. SHG has been applied both spectroscopically and in real-time to study H-terminated Si(100) during ion bombardment and (subsequent) XeF@sub 2@ etching using a fs Ti:sapphire laser. Low-energy (50-1000 eV) ion bombardment of c-Si results in a layer of amorphous silicon (a-Si) with a thickness of several nanometers and is expected to create defects such as dangling bonds and strained bonds in this damaged layer. For the applied fundamental photon energy range of 1.35-1.75 eV the SHG signal for c-Si is mainly governed by a two-photon resonance at 3.3 eV related to strained Si-Si bonds in the surface region. This resonance has been characterized before, during, and after ion-induced etching of H-terminated Si(100). It has for example been observed that the resonance at 3.3 eV substantially increases in amplitude during ion bombardment while an additional broad resonance at 3.2 eV seems to emerge. From comparison with spectroscopic ellipsometry studies and by XeF@sub 2@ dosing experiments, the former resonance is likely to originate mainly from strained Si-Si bonds at the a-Si / c-Si interface while the latter seems to be related to strained bonds in the a-Si surface region. Prolonged XeF@sub 2@ etching of a-Si and c-Si results in an almost complete quenching of the SHG signal, followed by a partial recovery of the SHG signal in which two separate resonances can be distinguished. The dynamics of the spectral SHG signal can aid in understanding the role of strained bonds in the Ar@super +@ and XeF@sub 2@ etching process of silicon.

9:40am **SS1-FrM5 157 nm Laser Interactions with Fused Silica@footnote 1@***, **S.R. John**, J.A. Leraas, S.C. Langford, J.T. Dickinson,* Washington State University

The F@sub 2@ excimer laser, with a wavelength of 157 nm and a photon energy of 7.8 eV, has been shown useful for micromachining a number of technologically useful materials and has potential applications in developing optics, resists, and scanners for DUV lithography. Two materials that have been examined extensively are fused silica and PTFE (Teflon). Little has been done to understand the detailed mechanisms underlying the superior etching behavior of these materials at 157 nm. Here we present a summary of our initial studies. Beginning at fluences well below threshold for plasma formation, we have examined the direct desorption of atomic ions from fused silica surfaces at 157 nm. We used time resolved mass spectroscopy to identify the species and determine their kinetic energies. Both Si@super +@ and O@super +@ are observed. Prolonged irradiation reduces the emission intensities, consistent with the consumption of defects by the emission process. Molecular dynamics simulations of the silica surface suggest that silicon ions bound at surface oxygen vacancies (analogous to E' centers) provide suitable configurations for emission. Direct emission involving antibonding chemical forces (Menzel-Gomer-Redhead model) are suggested as the origin of the observed kinetic energies. If time permits, results on PTFE will be presented, showing significant neutral and ion emissions (with high kinetic energies). @FootnoteText@ @footnote 1@This work was supported by the Department of Energy.

10:00am **SS1-FrM6 Ion-induced Initiation of Defects on Graphite at Hyperthermal Beam Energies***, X. Liu, **T. Tzvetkov**, X.D. Qin, D.C. Jacobs,* University of Notre Dame*; N. Mateljevic, J.C. Tully,* Yale University

Ion beams of O@super +@, O@sub 2@@super +@, and Ne@super +@ with incident energy of 5-20 eV are used to etch a Highly Oriented Pyrolytic Graphite (HOPG) surface. The study is focused on the initial stages of defect initiation when well-ordered HOPG is damaged by ion bombardment. The defects generated by the ion beam are observed with ex-situ Scanning Tunneling Microscopy (STM). The density and size of the defects are analyzed as a function of the dose, incident energy, and chemical identity of the ion. Kinetic Monte-Carlo simulations reveal that the probability of an incident ion removing a carbon atom from an intact basal plane are orders of magnitude smaller than removing a carbon atom from a site adjacent to a defect.

10:20am **SS1-FrM7 Etching of Carbonaceous Thin Films by Atomic Oxygen: The Influence of Chemical Composition, Substrate Temperature and Gas Phase Environment***, **H. Fairbrother**, J. Gorham,* Johns Hopkins University

The etching of carbonaceous thin films by atomic oxygen (AO) is an important component of many industrial plasma cleaning and decontamination strategies. AO is also the central species responsible for the degradation of polymers exposed to Low Earth Orbit (LEO). To improve the mechanistic understanding of AO mediated erosion processes, the surface reactions of AO with various carbonaceous thin films have been studied using X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscopy (AFM). In situ XPS analysis revealed that AO mediated erosion rates with carbonaceous films increase rapidly as a function of substrate temperature. This effect was correlated in part with the thermal stability of the oxidized carbon species produced as intermediates during the etching process. In low pressure plasma cleaning processes surfaces are typically exposed to a variety of reactive species. As an initial step towards identifying the existence and magnitude of co-operative effects between AO and other reactive species contained in plasma discharges results will also be presented on the erosion of carbonaceous thin films exposed simultaneously to AO and low energy (< 100eV) electrons. In these studies XPS analysis will be augmented by AFM studies, using HOPG as a model substrate for carbonaceous films. To identify their suitability as protective coatings for spacecraft vehicles exposed to LEO the surface reactions of AO with amorphous carbon phosphide films have also been examined. In these studies phosphorous incorporation was found to retard the rate of AO erosion due to the formation of a passivating surface layer that contains highly oxidized phosphorous species.

10:40am **SS1-FrM8 Consequences of Exposing Ionic Single Crystals to UV Laser Light, keV Electrons, and Low Pressure Water Vapor@footnote 1@***, J.T. Dickinson, K. Kjelgaard, **S.C. Langford**,* Washington State University

At low pressures, water often does not stick to clean, room temperature surfaces, including surfaces of insulating inorganic materials. Nevertheless sorption, including dissociative sorption, can be strongly enhanced by defects, such as atomic steps, vacancies, and adatoms. We have examined the consequences of exposing ionic, single-crystal surfaces simultaneously to energetic radiation (UV photons, keV electrons) and relatively low pressures of water vapor. Dramatic synergisms are observed, presumably due to chemisorption-induced bond weakening. We describe mechanistic studies of this phenomenon, including time-resolved measurements of the response of the radiation-induced particle emission to transients in water pressure (@DELTA@P@sub H2O@ 10@super -9@ to 10@super -5@ Pa). Both ion and neutral particle emission rates respond to these transients on time scales of micro- to milli-seconds. We use scanning electron and atomic force microscopies to image the surface modifications associated with this loss of material, beginning with the removal of single atomic layers along step edges and eventually yielding micron-scale pits. We present AFM evidence that material removal is highly localized and defect mediated. We suggest that radiation-induced defects produce atomic-scale structures along steps (e.g., kinks) that peel off when the associated chemical bonds are weakened by sorbed, water-derived radicals. Supporting evidence from spectroscopic and microscopic data on exposed surfaces will be presented. We also show novel nanostructures produced by exposure to energetic radiation in the presence of water vapor. @FootnoteText@ @footnote 1@This work was supported by the Department of Energy.

Surface Science
Room 203 - Session SS2-FrM
Electronic Structure of Surfaces

Moderator: J.G. Tobin, Lawrence Livermore National Laboratory

8:20am **SS2-FrM1 Three-Dimensional Valence Band Structure of WTe@sub 2@*, T. Ohta,*** Lawrence Berkeley National Laboratory/Fritz Haber Institute*; A. Bostwick, E. Rotenberg,* Lawrence Berkeley National Laboratory

We report complete valence band structure measurement of tungsten ditelluride (WTe@sub 2@) in 3-dimensions (3D) of k-space by angle-resolved photoemission spectroscopy (ARPES). WTe@sub 2@ is comprised of Te-W-Te layers, and is known to exhibit semi-metallic conduction. Unlike most transition metal dichalcogenide compounds, WTe@sub 2@ has an orthorhombic unit cell. It was previously shown by density-function-theory calculation that WTe@sub 2@ has a metallic band in addition to a semi-metallic band, which is brought about by W 5d and Te 5p bands overlapping near the Fermi-level (E@sub F@). So far, the parallel existence of semi-metallic and metallic bands has not been clearly demonstrated in photoemission experiments due to a complex overlap of W 5d and Te 5p derived states, and because of their k@sub z@ (k perpendicular) dependence near E@sub F@. To shed light on this issue, we have conducted complete 3D band structure mapping of WTe@sub 2@ using synchrotron radiation ARPES. 3D band structure mapping is a powerful tool for investigating the entire electronic structure of a material by visualizing valence band in all three k directions. We have clearly observed the semi-metallic and the metallic bands crossing E@sub F@, and the k@sub z@ dependence of both semi-metallic and metallic bands especially close to E@sub F@. While the semi-metallic band has a slight k@sub z@ dependence, the metallic band appears only near the zone center. We compare our measured 3D band structure to the reported band structure calculation with emphasis on the Fermi surface contour. The semi-metallic conduction can be attributed to the semi-metallic band existing throughout the k@sub z@ direction, whereas the metallic band is limited to the zone center.

8:40am **SS2-FrM2 High Resolution Angle Resolved Photoemission Study of the Electronic Structure of InN(0001)*, L. Colakerol,*** *L. Plucinski, S. Wang, H.K. Jeong, K.E. Smith, P. Chen, T.D. Moustakas,* Boston University

We report a study of the surface and bulk electronic structure of InN(0001) thin films using high resolution synchrotron radiation excited angle-resolved photoemission (ARPES).@footnote 1@ The InN thin films were grown by plasma-assisted molecular beam epitaxy on c-plane sapphire, and transferred in air to the synchrotron. Samples were cleaned both by annealing in UHV and by cycles of nitrogen ion bombardment followed by UHV annealing. Sharp 1 x 1 hexagonal LEED patterns were observed from the films following either cleaning procedure. Aside from the expected bulk valence band states, we have observed a series of unusual states near E@sub F@, in the bulk band gap, for a narrow range of excitation energies and band momenta. These states are free electron-like, with parabolic dispersion around the surface Brillouin zone center. The number of states observed is a function of annealing temperature, and these states are likely the result of segregation of In metal to the surface. Up to four individual states are observed, and we associate them with quantum well states due to an In metal overlayer. The states are insensitive to contamination by exposure to 1000 L H@sub 2@, and are not related to intrinsic surface states. Our results are discussed in the context of both the known surface electronic structure of GaN (0001),@footnote 2@ and of charge accumulation at InAs surfaces.@footnote 3@ @FootnoteText@ @footnote 1@ Supported in part by the NSF DMR-0311792, by U.S. ARO 40126-PH, and by U.S. AFOSR. Our spectrometer system is funded by U.S. ARO DAAD19-01-1-0364. Experiments performed at the NSLS which is supported by the U.S. DOE, Divisions of Materials and Chemical Sciences.@footnote 2@ Y.C. Chao, C.B. Stagarescu, J. Downes, P. Ryan, K.E. Smith, D. Hanser, and R.F. Davis, Phys. Rev. B 59, 15586 (1998).@footnote 3@ L.O. Olsson, C.B.M. Andersson, M.C. Haakansson, J. Kanski, L. Ilver, and U.O. Karlsson, Phys. Rev. Lett. 76, 3626 (1996).

9:00am **SS2-FrM3 Phase Diagram of Cr110 Thin Films Measured by ARPES*, E. Rotenberg,*** *B.K. Freelon, S.A. Morton, H. Koh, A. Bostwick,* Lawrence Berkeley National Laboratory*; K. Rossnagel,* Univ. Kiel, Germany*; A.K. Schmid,* Lawrence Berkeley National Laboratory*; S.D. Kevan,* Univ. of Oregon **INVITED**

We report the impact of dimensional confinement on physical properties associated with the spin-density wave (SDW) ground state in chromium. These properties are also of some technological importance since chromium is a common component of thin film magnetic structures. We prepared chromium (110) films of high crystalline quality on a W(110) substrate with a wedge-shaped thickness profile so that the impact of confinement can be systematically studied. We have characterized these films using a combination of low-energy electron diffraction and microscopy as well as high-resolution angle-resolved photoemission spectroscopy. By probing the Fermi surface and the nesting vectors that are relevant to the SDW ground state, we characterized the SDW incommensurability in the film directly, and we find that this incommensurability deviates markedly from the bulk value for thin films at higher temperatures: we find commensurate and incommensurate phases that are separated by nearly continuous transitions. Further changes in the SDW phase diagram arise upon hydrogen adsorbtion. Our results suggest a simple model to explain the delicate interplay between commensurate and incommensurate phases that involves a balance between SDW stabilization energy and surface and interface energetics.

9:40am **SS2-FrM5 Using Spin Resolved Resonant Photoemission to Probe Electron Correlations in Nonmagnetic Ce*, S.-W. Yu,*** Lawrence Livermore National Lab*; T. Komesu,* University of Missouri-Rolla*; B.W. Chung,* Lawrence Livermore National Lab*; G.D. Waddill,* University of Missouri-Rolla*; J.G. Tobin,* Lawrence Livermore National Lab

We have studied the spin-spin coupling between two f electrons of nonmagnetic Ce by means of spin resolved resonant photoemission. The two f electrons participating in the 3d5/2 to 4f resonance process are coupled in a singlet while the coupling is veiled in the 3d3/2 to 4f process due to an additional Coster-Kronig decay channel. Based on the Ce measurements, it is argued that spin resolved resonant photoemission is a unique approach to study the correlation effects, particularly in the form of spin, in the rare-earths and the actinides.

10:00am **SS2-FrM6 Localized Electronic States Around a Single Kondo Impurity from a First Principles Embedding Theory*, P. Huang,*** *E.A. Carter,* Princeton University

Scanning tunneling microscopy (STM) experiments of a single, magnetic adatom on non-magnetic metal surfaces reveal a sharp resonance in the immediate neighborhood around the adatom [e.g. Manoharan et al., Nature 403, 512 (2000)]. This intriguing observation has been interpreted as the presence of a "Kondo cloud", in which the localized d-electrons on the magnetic adatom hybridize with the metal band states to form an extended open-shell singlet near the Fermi level, thus effectively screening out the impurity moment. While the STM experiments have provided a first atomic-scale glimpse of this surface Kondo state, questions remain about the detailed electronic structure, and the nature of the low-lying excitations which give rise to the Kondo resonance width. We present a first-principles study of the electronic structure of a single Co adatom on Cu(111). Our approach is based on an embedding strategy [Kluner et al., PRL 86, 5954 (2001)], which views the Co adatom and nearest neighbor Cu atoms as a metal cluster embedded in a periodic slab background. The total Co/Cu(111) system is treated using density functional theory (DFT), which allows for a mean-field treatment of an extended periodic system. Using the DFT density for the total system, the effect of the background is cast into an effective embedding potential acting on the cluster. Explicitly-correlated theories (i.e. perturbation theory, configuration interaction) are subsequently applied to the embedded cluster in the presence of the embedding potential. The low-lying, many-body excited states are also treated within this same framework to yield excitation energies and wave functions.

10:20am **SS2-FrM7 Persistent Superconductivity in Ultra-Thin Pb Films: A Scanning Tunneling Spectroscopy Study*, D. Eom,*** *S. Qin,* The University of Texas at Austin*; M.-Y. Chou,* Georgia Tech*; C.K. Shih,* The University of Texas at Austin

We report a direct probe of the superconducting order parameter of superconducting crystalline Pb films in the ultra-thin regime (5 -18 ML) by using a home-built low temperature scanning tunneling microscopy/spectroscopy (STM/S). Surprisingly, we find that the 2D cooper pair condensates remain extremely robust down to the thinnest film (5ML) without any signature of the transition temperature (Tc) suppression. Moreover, we find that the quantum oscillations of order parameter are also very persistent in this regime and the oscillation correlates directly with the density of states (DOS) oscillation at the Fermi level. Finally a constant value of the ratio of energy gap to Tc close to that of the bulk was found, implying the same strong coupling nature for electron-phonon interaction. More detailed analysis of the interplay of quantum size effects and superconductivity will be reported.

10:40am **SS2-FrM8 Surface Electronic Transport in Ultrathin Silicon-on-Insulator*, P. Zhang*,** *E. Tevaarwerk, B. Park, D. Savage,* University of Wisconsin-Madison*; G. Celler,* Soitec USA*; I. Knezevic, P. Evans, M.A. Eriksson, M.G. Lagally,* University of Wisconsin-Madison

Silicon-on-insulator (SOI), a thin single-crystal silicon template layer on silicon dioxide, promises to become the platform for future high-speed electronics, as well as for a range of sensor technologies. When the Si layer is very thin, unique phenomena arise. The emergence of novel electronic properties with decreasing Si template layer thickness is particularly important. In contrast to the conventional view, ultrathin SOI displays rich electronic phenomena. It is usually claimed that STM imaging of thin SOI is impossible, because a thin SOI layer is fully depleted of free carriers (and thus overly resistive), which in effect eliminates the current path from the STM electrode tip to the contact. In complete contrast to this view, we report successful STM imaging of ultrathin (10 nm) SOI, when the top native oxide is removed and a clean reconstructed Si (001) surface is exposed.@footnote 1@ We explain theoretically the low sheet resistance of ultrathin SOI that has a reconstructed-Si [(2x1)] surface. We attribute the ability to image to surface electronic transport. The presence of a high density of states in surface bands (pi and pi*) and the position of the narrow surface bandgap are the dominant mechanisms in repositioning the Fermi level in ultrathin SOI. They lead to a high density of free carriers. The bulk doping density and the density of interface states on the back Si/SiO@sub 2@ interface are largely irrelevant for electronic properties of ultrathin SOI with a clean reconstructed surface. We confirm this conclusion with sheet resistance measurements on SOI covered with thin oxide. The influence of hydrogen on conductivity in ultra-thin SOI will also be discussed. Our measurements suggest that it will be possible to follow thin-Si-membrane structure and properties continuously from bulk to the ultimate limit of a Si film one unit cell high on oxide. Research supported by NSF, AFOSR, and DOE. @FootnoteText@ @footnote 1@Pengpeng Zhang, et al., submitted.

11:00am **SS2-FrM9 Using Nano-focussed Bremstrahlung Isochromat Spectroscopy (nBIS) to Determine the Unoccupied Electronic Structure of Pu***, M.T. Butterfield,* ***J.G. Tobin****, N.E. Teslich Jr., R.A. Bliss, M.A. Wall, A.K. McMahan, B.W. Chung, A.J. Schwartz,* Lawrence Livermore National Laboratory

The investigation of the actinides is of great interest because of their unique electronic structure. At the pivotal point of the behavior of the electronic structure of the actinide series is plutonium. Pu has the most complex phase diagram of all metals, both with regard to the intricacy of the crystal structures and the number of different phases. While there are a number of ongoing experimental efforts directed at determining the occupied electronic structure of Pu, there is essentially no experimental data on the unoccupied electronic structure of Pu. We aim to determine the conduction band (unoccupied) electronic structure of Pu and other actinides in a phase specific fashion and emphasizing bulk contributions by using Nano-focussed Bremstrahlung Isochromat Spectroscopy (nBIS). BIS is the high-energy variant of inverse photoelectron spectroscopy (IPES: electron in, photon out), which is essentially the time reversal of photoelectron spectroscopy (photon in, electron out). IPES can be used to follow the dispersion of electronic states in ordered samples. Owing to its low energies, IPES is usually very surface sensitive. However, by working at higher energies, we will sample preferentially for bulk properties, downgrading the impact of surface effects, following a philosophy similar to that of Mo et al.@footnote 1@ Thus, from BIS, we would have a direct measure of the conduction band or unoccupied electronic structure of the bulk Pu. By using a nano-focused electron source associated with a SEM, we hope to gather phase specific information from crystallites within polycrystalline Pu samples. We will discuss the experimental arrangement required to carry out such an experiment and our progress in building such a system. Acknowledgements :This work was performed under the auspices of the U.S. DOE by University of California, Lawrence Livermore National Laboratory under contract W-7405-Eng-48. @FootnoteText@@footnote 1@S.-K. Mo et al, Phys. Rev. Lett. 90, 186403.

Thin Films
Room 306 - Session TF-FrM
Thin Films on Flexible and Polymer Substrates

Moderator: J.M. Fitz-Gerald, University of Virginia

8:20am **TF-FrM1 Thin Film Electronics on Flexible Polymer and Steel Substrates*, S. Wagner*,** *I.-C. Cheng, S.P. Lacour, H. Gleskova, J.C. Sturm,* Princeton University **INVITED**

The flat panel display industry, growing rapidly, is developing flexible displays for its next technology generation. Flexible displays are attractive for light weight and resistance to fracture. They can be bent, conformally shaped, and possibly even stretched elastically. While the optoelectronic functions of flexible displays are similar to those of rigid displays, many of their materials, fabrication processes, and mechanics are new. We will concentrate on transferring the processes for display fabrication from glass plates to flexible substrates, and on the mechanics of flexible substrates. A manufacturer can choose from several display technologies, but only silicon is available for the transistors of the active-matrix transistor backplane. Therefore, the design of a flexible backplane begins with the selection of a foil substrate that is compatible with the silicon thin-film transistor process. The substrate may be an organic polymer or steel. It may need a planarization layer, and must have a layer that provides adhesion, chemical passivation, and electrical insulation. Converting from the chemistry of the substrate foil to the chemistry of a silicon nitride or silicon dioxide passivation layer enables the adoption of many processes developed for glass substrates. The mechanics of flexible substrates plays a role during processing, where it affects device film integrity and mask overlay alignment, and during post-process shaping. Shaping by bending is straightforward and is done in the elastic regime; the device films remain intact. Shaping to a spherical surface, or elastic stretching over an arbitrary surface, produce mechanical strain so large that devices break. A new physical architecture based on rigid device islands has been developed to prevent fracture. Flexible electronics offers a unique combination of materials, processes, devices, and mechanics.

9:00am **TF-FrM3 A Compliant System of Polyimide Microwires for Cryogenic Detector Applications*, C.A. Allen*,** *D. Franz, S.H. Moseley,* NASA Goddard Space Flight Center

We have developed a highly compliant, low thermal conductance system of electrical interconnects for cryogenic detector applications. The arrays of microwires are metallic thin film electrical leads supported by a layer of polyimide, capable of spanning the thermally isolated gap between the detector array and the cryogenic heat sink in cryogenic detector assemblies. The low thermal conductance of the microwires enables cryogenic detector thermal isolation without the need for conventional hard wiring, such as soldered manganin or stainless steel. Designed for compactness, an array of 30 microwires fits on a silicon chip less than one half of one square centimeter in total surface area. The free standing length of our microwires is measured in millimeters, as contrasted by units of microns for conventional air-bridge structures. Microwire arrays are terminated on each end by a solid silicon chip containing wire-bonding pads. The two ends of the chip are temporarily supported by a silicon frame, which is removed by laser dicing after the chip has been applied to the detector's thermal isolation platform. We describe techniques for fabrication of arrays of polyimide microwires with several different types of conductive traces, both superconducting and normal-metal. We will discuss their mechanical, electrical, and thermal properties.

9:20am **TF-FrM4 Hysteresis Behaviour during Reactive Sputtering using a Rotatable Magnetron*, D. Depla*,** *J. Haemers, R. De Gryse,* Ghent University, Belgium

Reactive magnetron sputtering is a widely used technique to deposit thin compound films on different types of substrates. On laboratory scale the use of a planar magnetron is common practice. However, on an industrial scale one prefers a rotatable magnetron as the target is consumed more efficiently. Unfortunately, detailed experimental results are scarce. Some authors have reported that the well known hysteresis behavior is influenced by the target rotation speed. To study this interesting phenomenon a small rotatable magnetron was developed with a cathode length of only 20 cm making a study on laboratory scale possible. In this paper we present the first results obtained with this device. As we have investigated reactive sputtering of aluminum oxide before using a planar cylindrical magnetron@footnote1,2,3@ this reactive gas/target combination was also used in this study. The discharge voltage was measured as function of the oxygen flow. First, the oxygen flow was increased stepwise until the discharge voltage decreases abruptly, indicating target poisoning. Then the oxygen flow was decreased stepwise. In this way, several hysteresis curves were measured. Two major conclusions can be drawn from these experiments. First, the critical flow to fully poison the target, i.e. when the discharge voltage decreases abruptly, shifts towards lower values with increasing rotation speed. Secondly, we notice that the critical flow to de-poison the target, i.e. when the discharge voltage abruptly increases, also shifts towards lower values with increasing rotation speed but the influence of the rotation speed is much stronger. As such, the hysteresis widens with increasing rotation speed. @FootnoteText@ @footnote 1@D. Depla, R. De Gryse, Plasma Sources Sci. Technol. 10 (2001) 547-555@footnote 2@D. Depla, R. De Gryse, J. Vac. Sci. Technol. A 20 (2002) 521-525@footnote 3@D. Depla, R. De Gryse, Surf. Coat. Technol. 138 (2004) 190-195.

9:40am **TF-FrM5 Bend Testing of OLED Devices on Polymer Substrates***, **J. Lewis**, S. Grego, E. Vick, D. Temple,* RTI International **INVITED**

The flexibility of organic light emitting diode (OLED) displays on flexible substrates is limited by the use of brittle inorganic films for components such as permeation barriers, transparent conductors, and TFTs. The development of a "rollable" display demands significant advances in the mechanical robustness of these brittle films. We will discuss advances in metrology techniques for the mechanical evalution of thin film components, including bend test and failure analysis methods. The fabrication of highly flexible displays requires not only highly flexible component films but also a well-designed display architecture, as layer-layer interactions can lead to mechanical effects not observed when bending components. We will report on the mechanical testing of OLED devices and demonstrate the effects of bending on the current-voltage characteristics, as well as inter-layer propagation of defects. We will discuss the potential impact of the mechanical failure of thin film components on overall device performance and robustness. This work was supported by the Army Research Laboratory (Contract No. DAAD17-01-C-0085).

10:20am **TF-FrM7 Magnetic Thin Film Media on Flexible Substrates by Vacuum Roll to Roll Magnetron Sputtering***, **J. Skorjanec**,* Imation Corporation, US*; C. Merton, M. Hintz,* Imation Corporation

Thin film magnetic media similar to thin film disk has been prepared on polymer substrates by magnetron sputtering in a vacuum roll to roll process. Initial samples to determine film composition, magnetics, and layer thicknesses were prepared in a coupon coater and then transferrred to the roll to roll coater. The roll to roll coater equipment will be described. Some effects of substrate type and deposition parameters on magnetic properties will be discussed. Single pass , multilayer films of long lengths(>300 ft) on polymer substrates were made with final magnetic properties equivalent to the coupon samples with Hc~3400 Oe and Mrt~1memu.cm2.

10:40am **TF-FrM8 Enhanced Properties of IZO Films Deposited on Polymeric Substrate Using Ion-beam Assisted Sputtering for Organic Light-emitting Diode***, **H.C. Pan**, C.Y. Su,* National Applied Research Laboratories, Taiwan, R.O.C.*; C.N. Hsiao,* National Applied Research Laboratories, Taiwan, R.O.C., Taiwan*; Y.-S. Chiu, J.-H. Jou,* National Tsing Hua University, Taiwan, R.O.C.

Zn-doped In@sub 2@O@sub 3@ (IZO) thin films with 5 and 10 wt.% Zn content were prepared on polymeric polyethylene terephthalate (PET) substrate using ion-beam assisted deposition (IBAD) at room temperature. A 15 nm-thick SiO@sub 2@ films were therefore deposited prior to IZO films on PET substrate act as passivation layer to prevent the movement of impurity from underneath layer. The deposited IZO films show amorphous structures with highly electrical conductivity, optical transmittance and surface smoothness on the PET substrate. The 10 wt.% IZO films deposited in a pure Ar atmosphere without IBAD show low resistivity of about 8x10@super -4@ @ohm@-cm, comparable to that of 5 wt.% IZO films (2x10@super -3@ @ohm@-cm). It is found that increase of IZO film thickness leads a high electrical conductivity and decrease of energy band gap regardless of the Zn content of IZO films. The IZO surface morphology increased smoothness with increasing the ion-beam voltage, while the 5 and 10 wt.% IZO film showed a surface roughness variation ranging from 1.7 nm to 1.5 nm and 2.1 nm to 1.5 nm, respectively. Both trends are consistent with more energetic growth condition that enhances the surface diffusion. The energetic contribution of ions with applied 90 V improves the crystallinity of 5 wt.% IZO thin films as shown by a (222)-diffraction peak in the XRD examination. The 5 wt.% IZO films exhibiting higher conducting distribution uniformity with IBAD was characterized using conducting atomic force microscopy (CFAM). The Al/Alq@sub 3@/IZO/SiO@sub 2@/PET stacks were evaluated for flexible organic light-emitting diode (OLED). OLED were fabricated with both 5 and 10 wt.% IZO film electrodes, and the OLED devices with 5 wt.% IZO electrode showed improved electrical performance due to its crystalline than that of 10 wt.% IZO films.

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